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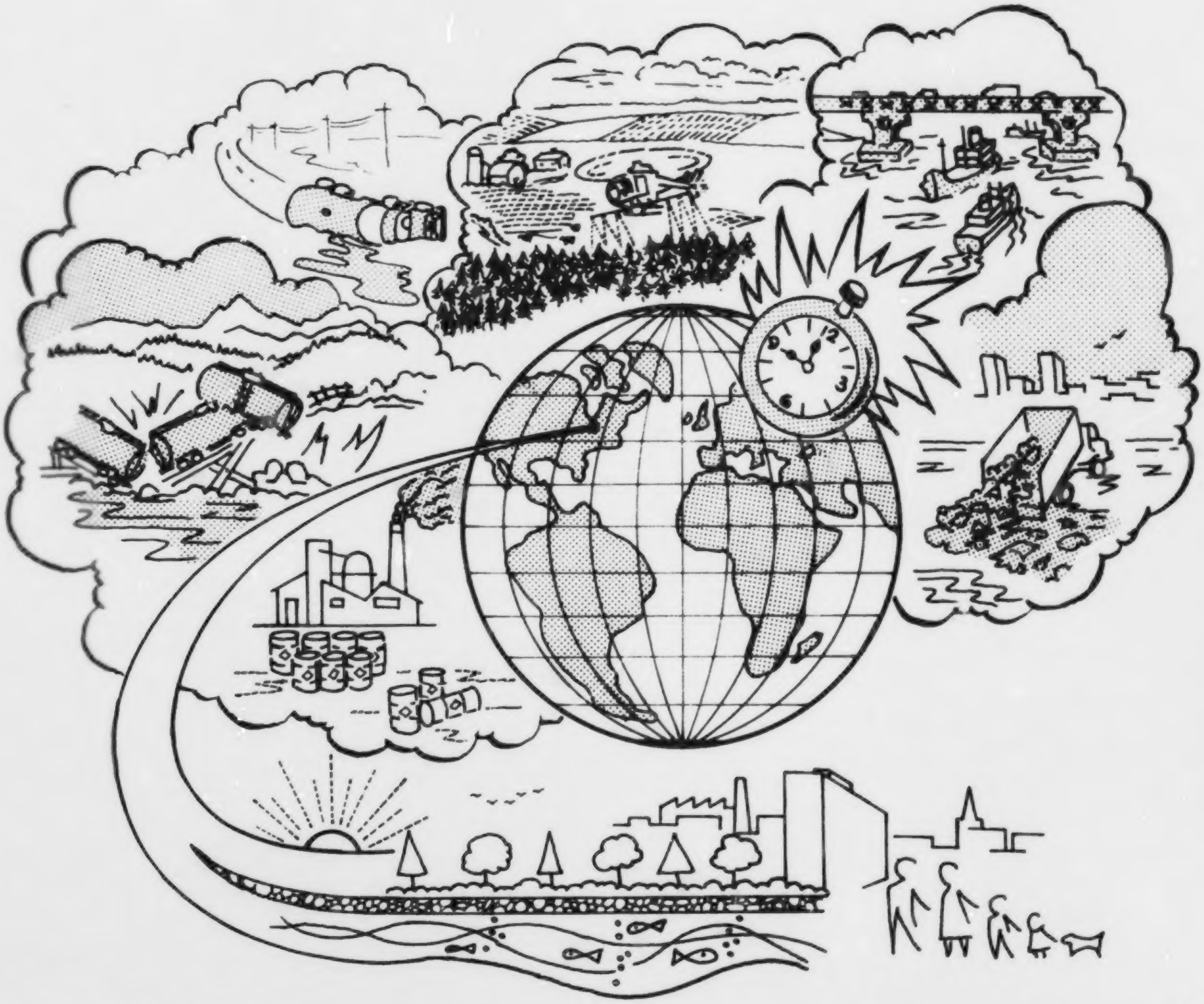

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PROCEEDINGS OF THE TECHNICAL SEMINAR ON CHEMICAL SPILLS

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EVAPORATION RATES OF CHEMICAL SPILLS

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INTRODUCTION.

When a liquid chemical is accidently spilled it is useful to be able to calculate or estimate the evaporation rate. This information can be used to estimate downwind air concentrations and the likely duration of the evaporation period. In some cases it may be best to evacuate the area and allow evaporation to disperse the chemical. In other cases evaporation may be so slow that another countermeasure should be implemented.

This issue has been addressed by several workers, for example Mackay and Matsugu (1973) Mackay et al. (1980) Stiver and Mackay (1983) and Drivas (1982).

In this paper we review briefly methods of calculating evaporation rates and we identify some problem areas.

THEORETICAL.

It can be shown that the evaporation rate of a liquid at a surface is given by

$$N = KAP/RT = (Vo/v)dF/dt$$

where
N is the evaporation rate (mol/s)
K is the mass transfer coefficient (m/s)
A is the spill area (m2)
P is the liquid's vapour pressure (Pa)
R is the gas constant (8.314 Pa m3/mol K)
T is the absolute temperature (K)
Vo is the initial spill volume (m3)
v is the liquid's molar volume (m3/mol)
F is the volume fraction evaporated
t is time (s)

Rearranging gives

$$dF/dt = (Pv/RT)(KA/Vo)$$

If we introduce a new variable θ as

$$\theta = KAt/Vo$$

and assume that K, A and Vo are constant then

$$d\theta/dt = KA/Vo$$

thus

$$dF/d\theta = (Pv/RT)$$

If, further Pv/RT is a constant designated H then

$$dF/d\theta = H$$

and integrating from t of zero when F is zero gives

$$F = H\theta$$

Clearly, evaporation is complete (for constant H) when $H\theta$ is unity.

The groups H and θ deserve some consideration. H is a dimensionless Henry's law constant or ratio of concentration in the vapour phase at equilibrium (P/RT mol/m3) to concentration of the liquid in the liquid (1/v mol/m3). Table 1 gives some selected values.

H is primarily a function of temperature and vapour pressure, high values corresponding to volatile liquids. It is a thermodynamic quantity unrelated to spill dimensions or to wind conditions.

θ is a dimensionless parameter termed the evaporative exposure. Since K is the vapour "piston velocity" and A is the area KA is the volume of vapour leaving the spill per unit time (m3/s) and KAt is thus the total vapour volume (at saturation conditions) which has been generated. Since Vo is the initial liquid volume θ is thus the ratio of (saturated) vapour volume generated to initial liquid volume.

The significance of the $H\theta$ product is thus

$$H\theta = \frac{(P/RT)}{(1/v)}\,\frac{(KAt)}{(Vo)} = \frac{\text{Vapour Conc.}}{\text{Liquid Conc.}}\;\frac{\text{Vapour Vol}}{\text{Liquid Vol (initial)}}$$

Since the product of concentration (mol/m3) and volume (m3) is amount (mol)

$$H\theta = \frac{\text{amount evaporated}}{\text{initial amount}} = F$$

Typical F-θ curves are given Figure 1 and 2.

θ is entirely a function of the spill dimensions and the prevailing wind conditions, which control K. Note that Vo/A is the spill mean thickness (m).

Assuming, for illustrative purposes that K is 0.01 m/s (i.e. 1 cm/s), that (Vo/A) is 0.001m (i.e. 1 mm) then

$$0 = 0.01t/0.001 = 10t$$

In one hour θ may reach a value of typically 36000 and in one day 864000. A useful rule of thumb is that for a 1 mm spill under moderately windy conditions θ increases at about 1 million per day.

Various values of F and the time necessary for complete evaporation of a 1 mm spill are also given in Table 1 assuming that θ is 10t as illustrated above. It is thus possible to calculate the spill duration and the emission rate, which is N or KAP/RT mol/s. This emission rate can be used as a source strength for a plume concentration calculation. N values are shown in Table 1 for a spill of area 100 m2.

This simple approach assumes constancy in K, A, v, T and P. In many cases these quantities vary and this simple solution breaks down. In such cases the spill evaporation rate is given by

$$dF/dt = (Pv/RT)(KA/Vo) = H.\theta/t$$

An analytical expression is thus necessary in which the variable quantity is expressed as a function of time or of F.

Spill dimension and environmental condition quantities K and A are best expressed as a function of time. For example if the spill spreads A could be expressed as

$$A = X + Yt$$

and this equation integrated to give

$$F = H\{(KXt/Vo) + KYt^2/2Vo\}$$

Clearly, evaporation will be complete faster because of the second term's contribution. The mean area which applies over a time period T is thus

$$X + YT/2$$

or the mean of the initial and final areas. As is intuitively apparent evaporation is a process in which rate is linearly related to area.

Similarly the evaporation behaviour is linear in K, which normally results from a change in wind speed. For approximate purposes it is thus acceptable to assume an average area and K for the time period of interest.

The term T in H is a density correction factor and varies little since a 10°C change alters T by only 3.5% at 15°C or 288 K. Much more important is the effect of temperature on vapour pressure P. If P changes linearly with time an average value of P applies, but if T changes linearly with time P varies non linearly and an average value is no longer appropriate. The best approach to account for temperature variation is to calculate the P variation then select some average value of P.

The correct average quantity is

$$(1/t)\int_0^t P(t)dt$$

where P(t) is the expression for pressure as a function of time.

More difficult is the situation in which the liquid is a mixture thus P and v vary with composition. Examples are gasoline, mixed solvents and aqueous solutions of acids or ammonia. The best approach is to develop an expression for P and v (combined in H) as a function of F. We have discussed such situations in a recent report (Stiver and Mackay 1983) and have suggested the use of an expression of the type

$$\ln H = \ln Ho - BF$$

where Ho is the initial Henry's Constant, i.e. of the fresh liquid ($F=0$) and B is a constant. In some cases Ho and B can be estimated from the boiling point-composition curve of the mixture. For several crude oils the relationship applies

$$\ln H = 6.3 - 10.3(To + TgF)/T$$

$$=(6.3 - 10.3To/T) - (10.3Tg/T)F$$

$$\text{thus } \ln Ho = 6.3 - 10.3To/T$$

$$B = 10.3Tg/T$$

where To is the initial boiling point (K) and Tg is the slope of the boiling point - F curve, i.e. the final boiling point ($F=1$) is ($To + Tg$). T isthe temperature of evaporation.

Now since

$$dF/d\theta = H = \exp(\ln Ho - BF)$$

integrating with the initial condition that F and O are zero gives

$$F = \ln(1+BHo\theta)/B$$

If B is small, i.e. the vapor pressure rises only slightly, this reduces to the previous equation and again

$$F = HoO$$

This equation can be used to estimate F at any desired value of θ. The important conclusion is that the term B contains an allowance for the decreasing vapour pressure of mixtures.

EXPERIMENTAL APPROACHES.

There are two approaches for obtaining experimental information a about evaporation characteristics of chemicals under environmental conditions.

First is to evaporate the chemical in a tray with a constant wind speed. For a pure chemical F will rise linearly and will reach unity (evaporation is complete) when θ is 1/H. The slope of the line dF/dθ is H. To evaluate H, θ must be known, thus K must be measured by repeating the experiment under identical conditions with a substance of known H. Toluene is a convenient substance with well documented P and v (and hence H) values. For a mixture the F-θ line is curved and values of Ho and B must be fitted. The initial slope dF/dθ is Ho. Trial and error solution can be used to estimate B.

Second is to evaporate the chemical by bubbling air through a sparger into a long (>10 cm) column of liquid chemical such that the exit vapour is saturated. The evaporation rate is the GP/RT where G is the exit gas rate (m3/s) which can be measured with a gas meter. θ can then be shown to be Gt/Vo since G is exactly analogous to KA. A plot of F versus time can be transformed into a plot of F versus θ yielding the same curve. This approach is more accurate since no estimate of K is needed, but the evaporation process is slow. Typically it takes 1 day for a θ of 5000, a factor of 200 slower than a tray evaporation system.

Gas stripping is thus preferred for systems in which H is 1/50000 or higher, but tray evaporation is better for lower values of H.

It is of course essential that the experimental determinations be done at the appropriate controlled temperature. A family of F-θ curves can be generated at various temperatures.

DISCUSSION.

This evaporation theory is well established and can be used with some confidence. There are however three probelem areas.

Values of K

Although several correlations for K have been published (e.g. Mackay and Matsugu (1973) Mackay and Yuen (1983)) there remains some doubt about the dependence of K on wind speed, molecular weight or Schmidt No., and pool size (or fetch). More confirmatory data is needed covering a range of temperatures, wind speeds and Schmidt Numbers.

Wet Bulb Effect

When a volatile liquid evaporates, it cools to a lower "wet bulb" temperature, at which there is a balance of heat input to satisfy the needs for enthalpy of evaporation. An extreme case is liquefied natural gas evaporation. There is not an adequate treatment of situations which are intermediate between such cryogenic liquids and slower evaporating liquids such as gasolines. This aspect is particularly important because Canadian environmental temperatures regularly range from -30°C to +30°C, thus the wet bulb effect is dependent not only on the substance, but also on the conditions. "Gases" such as ammonia or vinyl chloride can be liquids under some Winter conditions. It would be very valuable if nomographs or rapid calculation schemes could be devised to cover such situations.

Absorption

If the liquid is absorbed or adsorbed into or onto a porous surface such as soil or snow, much of it is shielded from the atmosphere and evaporation rates are reduced significantly. Although there is a considerable literature on pesticide evaporation from soils there is a paucity of information on evaporation rates from soils and snow. Even penetration into soil and snow is not well characterized. Again nomographs are desirable.

It is apparent, however, that with the widespread availability of low cost portable computers it should be possible to generate rapid reliable estimates of evaporation characteristics. The required data on physical-chemical properties can be obtained readily from the TIPS manuals of Environment Canada or from Handbooks. Careful design of such programs is necessary to ensure that units are consistent, that default values are selected only when necessary and when selected are assigned reasonable values. It is also possible to calculate downwind concentrations using plume dispersion equations.

CONCLUSIONS.

The theory of the evaporation of liquid chemicals spills is well established. The key variables are a Henry's Law Constant (H) and an evaporative exposure (θ). From a knowledge of these quantities the evaporation rate can be calculated as can the duration the spill incident, i.e. until evaportion is complete.

The major difficulties are (i) quantification of the evaporation mass transfer coefficient K, (ii) characterizing of the wet bulb effect and (iii) treatment of situations in which the liquid is partially absorbed into soils or snow. Perhaps the aim should be to devise simple nomographs or algorithms to describe such situations which can be incorporated into computer models and which can be used at the scene by response personnel.

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Stiver and Mackay Spill Tech Newsletter.

TABLE 1

Compound	Temp (C)	v m3/molx10^6	P Pa	H x10^6	F 0.1h	after 1.0h	Evap Time (s)	N mol/s
n-hexane	15	130	12900	700	1.0	1.0	140	55
n-octane	15	162	1040	70.6	0.25	1.0	1400	4.4
n-decane	15	195	82.6	6.71	0.02	0.24	15000	0.34
n-dodecane	15	227	6.23	0.591	0.002	0.02	170000	0.026
toluene	5	106	1230	56.3	0.20	1.0	1800	5.3
	15	106	2210	97.8	0.35	1.0	1000	9.2
	25	106	3790	162	0.58	1.0	620	15
acrylonitrile	25	65.8	15200	404	1.0	1.0	250	61
water	20	18	2340	17.3	0.06	0.62	5800	9.6
1-octanol	20	177	6.61	0.480	0.002	0.017	210000	0.027

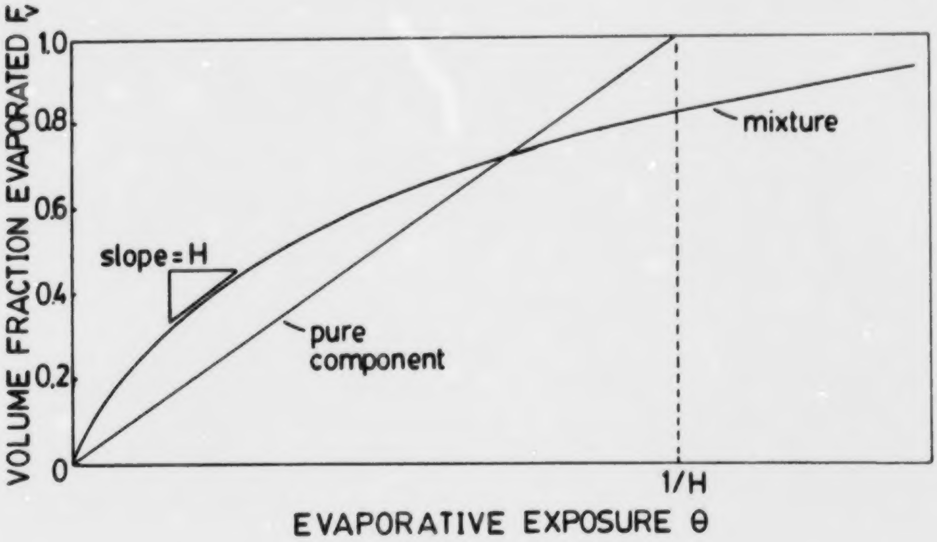

Figure 1 Illustrative graph of F_v versus Θ.

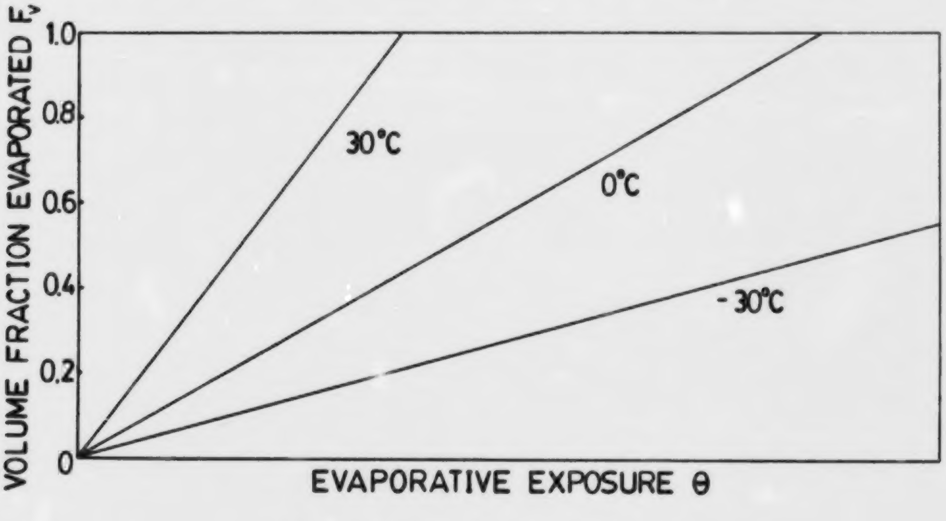

Figure 2 Effect of Temperature on $F_v - \Theta$ graph.

COMPARISON OF CONVENTIONAL CHEMICAL SPILL AIR AND WATER DISPERSION MODELS

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ABSTRACT

Two established computerized air dispersion modelling systems for chemical spills have been compared with a computer-generated nomogram system that was developed recently to estimate hazard zones of chemical spills for the purpose of contingency planning. These models - HACS (U.S. Coast Guard), SPILLS (Shell Oil Co.) and TIPS (Environmental Protection Service) - are all based on conventional Gaussian diffusion formulations. The performance of these models has been compared with one another for several chemicals (benzene, chlorine, propylene and vinyl chloride) and the predictions of the HACS and TIPS models have been compared with experimental field data from controlled LNG spills conducted by Lawrence Livermore Laboratory at the China Lake test site.

The water dispersion components of TIPS and HACS have been compared for benzene, ethylbenzene, chlorine, vinyl chloride and tetraethyl lead. The processes modelled were venting, spreading on water, evaporating and spreading, mixing and dilution, and sinking.

Agreement among the air dispersion components was generally within a factor of two or better. Where direct comparisons were possible, the TIPS and HACS water dispersion components produced essentially equivalent results. The mixing/dilution and 'insoluble sinker' components of TIPS offer improvements upon HACS.

Results of the comparative calculations and their implications are discussed.

1.0 INTRODUCTION

Techniques for simulating (modelling) the movement of chemicals in various media (air, land, water) are important for the purposes of responding to accidental releases of hazardous chemicals and for evaluation of potential impacts from various possible chemical spills. In this connection, Environment Canada has sponsored the production of manuals containing Technical Information for Problem Spills (TIPS), in which nomograms have been developed for the prediction of chemical concentrations away from the spill site (TIPS, 1982). It is important that the methods utilized in the TIPS manuals be compared with other models and experimental data. For this purpose the present study was conducted under the sponsorship of Environment Canada.

This paper describes the results of the study and includes the inter-model comparisons for the dispersion in air of four chemicals: (benzene, chlorine, propylene and vinyl chloride), spills on water of ethylbenzene, chlorine, benzene, vinyl chloride and tetraethyl lead as well as comparisons with experimental air dispersion data (China Lake LNG spill experiments, Koopman et al., 1981, Ermak et al., 1981). More specifically, the size of the predicted hazard zones based on a certain concentration limit are considered. The hazard zone concentration limits in air are taken as the lower value of 10 times the Threshold

Limit Value (TLV●) for hazardous chemicals or the Lower Flammable Limit (LFL) for flammable chemicals.

● Registered trademark of American Conference of Governmental Industrial Hygienists

2.0 THE AIR DISPERSION MODELS AND THEIR PRESENT APPLICATION

Two models were chosen for comparison with TIPS. These are the U.S. Coast Guard HACS model (Potts, 1981) and the Shell SPILLS model (Fleischer, 1980). All models are available as computer programs (TIPS is partially computerized) and all are based on simple Gaussian formulations for dispersion of passive contaminants in an infinite medium (air for this part of the study). HACS and TIPS may also be used for dispersion in water, which is addressed in later sections of the paper. Of these three models, only TIPS has the option of specifying either an instantaneous (puff) release into the atmosphere or a continuous (plume) release. The air dispersion comparisons refer to spills on either water or land.

One of the most important parameters affecting the size of hazard zones is the rate of release of vapour to the atmosphere. For the estimation of the vapour release rate, the TIPS method (when the plume option is chosen) uses the correlations developed by Mackay and Matsugu (1973). However, TIPS uses a default value for the wind speed used in the vapour release rate calculations based on an average of mean annual windspeeds at points across Canada (4.5 m/s), whereas SPILLS and HACS use the input wind speed for this purpose. Hence, for comparison purposes, all the models were run for a given sample spill scenario, once as one would normally use the models, and once by adjusting the wind speed (for TIPS), the ambient temperature (for SPILLS and HACS) and/or the spill area (HACS), so that the vapour release rates match among the models. Note that this consideration only arises for chemicals like benzene with a relatively slow evaporation rate.

The experimental data chosen for comparison with TIPS were the China Lake Burro Series LNG spill test data (Koopman et al., 1981; Ermak et al., 1981). In these experiments, 40 m^3 of LNG were spilled from a reservoir-pipe arrangement onto the surface of a pool of water, and the concentration fields downwind were measured. Of the nine separate experiments, only four were extensively reported on, and only two of these four (Burro 7 and 9) were amenable to direct comparison with TIPS, since the TIPS program is designed only for neutral and moderately stable (D and F) atmospheric stability conditions for purposes of conservatism. Hence TIPS and HACS were run for the conditions of these two experiments for comparison purposes. SPILLS was not included since LNG is not one of the chemicals in the SPILLS data file.

Other experimental data on LNG spills are also available, however either on a much reduced scale (Koopman et al., 1980), or from laboratory wind tunnels (see Meroney and Neff, 1982, for a short bibliography and recent data). Comparison of TIPS predictions with such data has not been undertaken for the purposes of the present study which is concerned with more realistic and large-scale spills.

3.0 RESULTS OF AIR DISPERSION MODEL COMPARISONS

The results of model predictions for inter-model comparison purposes are summarized in Tables 1 - 4 for the chemicals benzene, chlorine, propylene and vinyl chloride, respectively. The results for predictions versus field data are summarized in Table 5. The values reported are the maximum downwind hazard distance from the source (from the area source if a pool is involved), X_{max}, and the maximum half-width, $(W/2)_{max}$, of the hazard zone.

Two sets of values are given for TIPS, one derived using the nomograms, the other obtained from a computer run. The input data for all the runs are given in the project report. For inter-model comparison purposes, the input data represent a spill scenario with a spill volume of 80,000 l, a windspeed of 2.1 m/s, and an ambient temperature of 20° C. Two atmospheric stability classes are considered: D class and F class. For comparison against field data, the input data are based on actual experimental conditions. Further details are given as notes in the tables. Discussion of these results is presented in the next section.

4.0 DISCUSSION OF AIR DISPERSION RESULTS

Examination of the results for benzene summarized in Table 1 indicates that the performance of the dispersion modules of all the models is quite similar for the plume spill scenario considered (comparing the adjusted values for TIPS with the unadjusted values for SPILLS and HACS, and vice versa). The differences arise due to the calculation of the vapour release rate and a factor of 2 is within expected bounds of agreement. In all cases, the unadjusted TIPS results (which would be obtained if one were to use the model with the given default values) are the most conservative, because of the built-in assumptions. However, such conservatism of the unadjusted TIPS relative to SPILLS and HACS is reduced if the wind speed at the time of the spill is much larger than the default value of 4.5 m/s used in the TIPS evaporation rate calculations in the case of continuous spills. Using benzene as a test case, for example, the hazard zone predicted by TIPS is slightly smaller than that predicted by SPILLS for wind speeds greater than about 9 m/s. Hence, the TIPS algorithm for calculating this rate might be modified to use the input wind speed, particularly if the wind speed is considerably higher than 4.5 m/s.

In the cases of chlorine, propylene, and vinyl chloride (Tables 2 - 4, respectively), where evaporation rates are much faster than that of benzene, the hazard zones predicted by SPILLS were much smaller than HACS, which, in turn, were comparable to but again smaller than TIPS. Hence TIPS predictions were the most conservative. SPILLS does not handle well chemicals with rapid release rates (i.e. less than 10 seconds to evaporate completely). In fact, it was not possible to run the SPILLS model at all for Class F stability condition for vinyl chloride.

Comparison of TIPS and HACS predictions with China Lake LNG data indicates that in one case (Burro 7) TIPS results are 2.5 - 4 times the measured downwind hazard distance, and HACS predictions are within a factor of 2 of the data. However, in the second case (Burro 9), TIPS predicts ~2 times the measured hazard zone whereas HACS predictions are about half of the measured data. Hence, although TIPS looks overly conservative in the first case, it is more consistent than HACS when the second case is considered.

It should be noted here that one other China Lake experiment (Burro 8) has been considered in the present study because the identified stability class during that experiment was E class, and it was thought that perhaps by taking the average of model predictions for D and F classes one would get at least an estimate of the hazard zone. Unfortunately, the atmospheric conditions during the experiment were such that the plume had bifurcated, and a much wider hazard zone was created than was predicted by TIPS (~250m vs ~50m) which can only handle single plume dispersion. This experiment hence points out one of the limitations of all of the current conventional models.

TABLE 1

Model Intercomparison of Predicted Hazard Zone Sizes for Benzene

	TIPS		SPILLS		HACS	
	D class	F class	D class	F class	D class	F class
X_{max} (km)	~ 1.5*		2.2		2.4	
	~ 5 (5.4)					
		~ 7*		6.9		9.5
		~ 21 (21)		19.2**		17.9**
$(W/2)_{max}$ (m)	~ 195*		150		160	
	~ 285 (260)					
		~ 275*		180		210
		~ 420 (365)		380**		340**

Notes:- TIPS values are nomogram derived (hence the ~ sign) assuming a plume type release; computer calculated values are given in brackets.

- Entries marked with * and ** are adjusted values:

* TIPS results calculated using a windspeed of 2.1 m/s instead of the default 4.5 m/s in evaporation rate calculation.

** SPILLS and HACS results calculated by adjusting the evaporation rate to match that of unadjusted TIPS. HACS results also contain an adjustment for the spill area.

TABLE 2

Model Intercomparison of Predicted Hazard Zone Sizes for Chlorine

	TIPS		SPILLS		HACS	
	D class	F class	D class	F class	D class	F class
X_{max} (km)	~ 40 (39.2)	> 100	11.4	42.4	28	> 100
$(W/2)_{max}$ (m)	~ 1900 (1780)	NA	1000	1400	1345	2000

Notes:- TIPS values are nomogram derived assuming a puff release; computer calculated values are given in brackets.

TABLE 3

Model Intercomparison of
Predicted Hazard Zone Sizes for Propylene

	TIPS		SPILLS		HACS	
	D class	F class	D class	F class	D class	F class
X_{max} (km)	~ 1.3 (1.3)	~ 3.5 (3.6)	0.43	0.75	0.70	~ 2.2
$(W/2)_{max}$ (m)	~ 90 (90)	~ 105 (105)	80	90	75	80

Notes:- TIPS values are nomogram derived assuming a puff release; computer calculated values are given in brackets.

TABLE 4

Model Intercomparison of Predicted Hazard Zone Sizes for Vinyl Chloride

	TIPS		SPILLS		HACS	
	D class	F class	D class	F class	D class	F class
X_{max} (km)	~ 10 (9.5)	~ 31 (32.0)	1.1 5.5*	NA	6.9	21.1
$(W/2)_{max}$ (m)	~ 535 (525)	~ 705 (695)	260 525*	NA	395	495

Notes:- TIPS values are nomogram derived assuming a 25% puff release; computer calculated values are given in brackets.

NA: SPILLS could not be run for F class, therefore output data not available.

* : When SPILLS was run using a smaller pool area (1500m^2) under the same conditions.

TABLE 5

Comparison of Predicted Hazard Zone Sizes for LNG against China Lake data

Burro 7 (D Class)

	China Lake Data	TIPS	HACS
X_{max} (m)	200	~ 800 (840)	345
$(W/2)_{max}$ (m)	20	~ 55 (59)	35

Burro 9 (D class)

	China Lake Data	TIPS	HACS
X_{max} (m)	330	~ 700 (695)	160
$(W/2)_{max}$ (m)	35	~ 50 (50)	15

Notes:- TIPS values are nomogram derived assuming a puff release; computed values are given in brackets.

5.0 THE WATER DISPERSION MODELS AND THEIR PRESENT APPLICATION

5.1 Introduction

Comparative modelling has been undertaken relative to the algorithms used for Environment Canada's TIPS manuals. Methods employed in development of TIPS nomograms for spreading, mixing and dilution of chemicals in non-tidal rivers and in lakes are based primarily on the approach and data in the manual treatment of CHRIS[1] and the HACS model. While the actual HACS model was not available for TIPS nomogram preparation, the theoretical basis for the model as outlined in the Assessment Models Handbook (AMSHAH) was adopted for development of the nomograms. Consequently, comparative modelling with the actual HACS model, as undertaken for this study, is expected to provide similar results, since HACS is essentially the computerized version of these manual methods.

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[1] CHRIS (Chemical Hazards Response Information System) developed for the U.S. Coast Guard, is designed to provide essential information for decision making during emergencies involving the water transport of hazardous chemicals. HACS (Hazard Assessment Computer System) is a basic part of that system.

TIPS nomograms for estimation of the zone of contamination for insoluble sinking chemicals was based on a model developed by L.J. Thibodeaux at the University of Arkansas. The theoretical basis for the Thibodeaux model varies significantly from the HACS model, with corresponding differences in results. The Thibodeaux model was selected for TIPS because of its sound theoretical basis, which has been confirmed by experimental data.

5.2 Methodology

The HACS and Thibodeaux models are simply mathematical descriptions of physical processes. The modelling of a chemical spill in the natural environment is a complex problem. Typically several processes are occuring at the same time. Computer modelling frequently requires simplifying assumptions to be made and often considers only one process at a time. Nomograms prepared for the TIPS manuals consider the following processes:

- venting from a tank car
- spreading on water surface
- evaporation and spreading coincidentally
- mixing and dilution in water
- sinking in water

Several assumptions were made to simplify computations for these processes. For example, with the exception of the venting and sinking models, all spills were assumed to occur instanteously. Chemicals were also treated as being either soluble or insoluble (i.e. rate of dissolution was not considered in TIPS). Chemicals with solubilities of < 0.1g/100 ml were treated as insoluble. Slightly or moderately soluble chemicals were assumed to dissolve completely, even if evaporation was taking place at the same time. On the other hand, the maximum pool radius for a floating chemical with low solubility was calculated assuming no dissolution. These assumptions not only simplified computations, but tended to maximize the pollutant hazard for any given process, thus presenting a worst case situation. Consistent with this approach, temperatures of the water/chemical were normally assumed at the maximum likely to occur for Canadian climatic conditions. For this study, the TIPS nomograms were compared with computed results using the HACS model. Illustrative examples have been taken directly from the TIPS manuals.

6.0 COMPARATIVE WATER DISPERSION MODELLING RESULTS

6.1 Comparison of similar modules in TIPS and HACS

The following comparative calculations were made using TIPS and HACS:

a) venting from a tank car (ethylbenzene and chlorine)
b) spreading on water - no evaporation (ethylbenzene)
c) simultaneous evaporation and spreading on water (benzene and vinyl chloride)

The results produced by TIPS and HACS for all of these processes and chemicals were essentially identical.

6.2 Mixing and Diluting in Water

When a soluble or water-miscible liquid is spilled on a water surface, mixing takes place and the spill is diluted. In streams and rivers, the mixing is caused by mass convection resulting from stream turbulence. The phenomenom of mixing is generally described by classical diffusion equations with one or more diffusion coefficients. These equations are applicable to neutrally buoyant liquids and solids that dissolve in water. Nomograms prepared for the TIPS manuals were based on equations presented in the Assessment Models Handbook (Phani

1974) for the 'far-field' approximation. That is the results are applicable sufficiently far downstream from the spill where the pollutant is spread uniformly throughout the river cross-section.

Documentation in support of the HACS model (Phani 1974) suggests that either 'far-field' or 'near-field' approximation can be used. The 'near-field' approximation assumes that the pollutant is not evenly distributed throughout the river cross-section and diffusion coefficients are defined in three dimensions. The 'near-field' approximation can be extended as far downstream as desired, but is particularly useful in defining pollutant concentrations in the initial stages of dispersion, before the spill has spread throughout the river cross-section.

The 'far-field' approximation was selected for TIPS for the following reasons:

- the general algorithm for 'far-field' pollutant modelling appears suitable for most rivers which are not very wide.

- the model is relatively simple to understand and apply; a single longitudinal dispersion coefficient is required to define the uniform concentration across the river.

- the time period recommended for transfer from 'near-field' to 'far-field' suggests that the 'far-field' approximation is suitable for most rivers at a reasonable distance downstream. The standard sample problem in the TIPS manuals is within the 'far-field' regime.

Unfortunately, the HACS model does not allow comparison of results used in TIPS for the 'far-field' approximation. While the HACS model was originally programmed for both cases, only the 'near-field' option is included in the version of HACS made available to the study team. This change was introduced by the model developer (R. Potts, private communication) because of a significant discontinuity in the results of the 'far-field' and 'near-field' approximations at the point of cross-over. No field or laboratory data appear to be available at this time to determine which algorithm is best. Further work by the model developer has not yet clarified this issue.

The 'near-field' approximation in HACS produces much higher pollutant concentrations (75 to 100 times for the standard TIPS sample problem) than the 'far-field' results, at the designated cross-over point. The 'near-field' results approach the 'far-field' results much farther downstream and in-fact fall below the 'far-field' results at very great distances from the spill. Obviously, further research is warranted on this aspect of pollutant modelling in future.

6.3 Sinking in Water

The spill of a high-density, insoluble liquid on water results in a zone of contamination along the stream bed. The extent of the zone of contamination depends on the characteristics of the spill and of the watercourse.

Nomograms prepared for the TIPS manuals were based on a model developed for the U.S. Department of Transport by Thibodeaux and Christy at the University of Arkansas (Thibodeaux 1980). According to the model developers, this model was intended for inclusion in the HACS model.

Both the HACS and Thibodeaux models appear to have individual strengths and weakneses. HACS tends to consider the size of the contamination zone essentially as a bottom spreading problem and appears most applicable to shallow rivers where the spill is assumed to reach the streambed very quickly. On the other hand, the Thibodeaux model considers in detail the range of droplet sizes produced by a given tank rupture size, together with their respective fall velocities in water. The zone of contamination is heavily dependent on the droplet fall velocity and the depth and velocity of the river. For deeper rivers, the zone of contamination predicted by the Thibodeaux model is significantly larger than results obtained from the HACS model.

The Thibodeaux model was selected for the TIPS nomograms because it is supported by experimental data. No similar supportive data is available for the HACS model.

Comparative results of the two models are provided in Table 6 for both a shallow and deep river. The example is based on a 20 tonne spill tetraethyl lead.

TABLE 6

Sinking of An Insoluble Liquid in Water

i) Case 1 - 10 m Depth

Assumptions	HACS	TIPS
Stream width (m)	250	250
Stream depth (m)	10	10
Average stream velocity (m/s)	0.5	0.5
Equivalent diameter of rupture (mm)	n/a	200

Results	HACS	TIPS
Sinking time (minutes)	0.7	18
Distance travelled before smallest particles reach streambed (m)	20	570
Equivalent width of contamination zone (m)	34	55

ii) Case 2 - 2 m Depth

Assumptions

Stream width (m)	100	100
Stream depth (m)	2	2
Average velocity (m/s)	0.5	0.5
Equivalent diameter of rupture (mm)	n/a	200 mm

Results

Sinking time (minutes)	0.1	4
Distance travelled before smallest particles reach streambed (m)	4	120
Length of contamination zone (m)	258	120
Equivalent width of contamination zone (m)	26	27

6.4 Water Dispersion Models - Conclusions

Nomograms prepared for Environment Canada's TIPS manuals for venting, spreading, simultaneous spreading and evaporation and mixing and dilution of chemical spills in water are based primarily on the approach and data in CHRIS and the HACS model. As expected, comparison of the TIPS nomograms with results from the HACS model are generally consistent and in very close agreement.

The exception to this is the mixing and dilution model. For the TIPS manuals, the 'far-field' approximation was used in accordance with the documentation in the Assessment Models Handbook (Phani 1974). Since only the 'near-field' option is now available in the HACS model, no direct comparison of 'far-field' results from TIPS and HACS was possible. Due to a significant discontinuity in the 'near-field' and 'far-field' results at the point of cross-over, the anticipated pollutant concentrations vary widely for the two methods. Unfortunately, no laboratory or field data are available to support either approach. Further research is needed in this aspect of pollutant modelling, with verification from actual spills.

TIPS nomograms for sinking of an insoluble liquid in water were based on a model developed by Thibodeaux at the University of Arkansas. The model is well documented and is supported by experimental data. Comparison of modelling results from the Thibodeaux and HACS models, suggests that the Thibodeaux model predicts a significantly larger zone of contamination for deep rivers. This results from its treatment of spill droplet size, fall velocity and downstream transport by moving water, whereas the HACS model is essentially a bottom spreading model.

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Identification of Hazardous Material Combustion Products: Protocol Development

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Abstract

A significant amount of research is being conducted to determine the nature of particulate borne emissions from the combustion of synthetic solids. However, surprisingly little effort has been devoted to the characterization of emissions from liquid chemical fires. A 2-phase study was initiated to develop a method to evaluate the particulate borne emissions from railroad tank car fires. The first phase involved the development of a furnace and analytical protocol for determining the products of combustion for several commonly carried commodities under conditions of varying oxygen availability as well as product consumption rates under ambient conditions. The second phase involved combustion of model compounds under controlled conditions. It was assumed that the expected environmental pressure fluctuations of plus or minus 5 to 10 Torr would have a negligible effect and could be ignored (i.e. that all fires would occur at an ambient pressure of one atmosphere). Thus, relative humidity and availability of standard air were the two principal variables in this experiment. In order to relate to actual accidents, the combustion apparatus described in this paper was designed to emulate the various conditions under which tank car fires may occur. This paper presents a detailed description of the combustion apparatus designed as well as the collection and analytical methods used to characterize the combustion products of a set of model compounds.

Introduction

When a chemical accident involves fire, a frequently discussed response option is to let the chemical burn. To justify this decision, a number of factors must be considered. Aside from the safety considerations, the relative hazards from smoke as opposed to unburned vapors must be taken into account. Additionally, a method is needed to more accurately predict the expected duration of a chemical fire.

A review of the literature revealed that data concerning the composition of chemical fire emissions are often dated and the result of conjecture rather than actual observations. Furthermore, published product consumption rates for chemical fires are the result of either theoretical calculations or measurements collected from "pool fire experiments". These data are not easily related to the product behavior in tank car fires.

The principal concern in this work is to evaluate the particulate-borne emissions and product consumption rates under conditions simulating those present when a transportation container is punctured and the product is on fire. This study was divided into two distinct parts. Part I was the design and construction of the analytical protocol and test apparatus. Part II is the generation and analysis of combustion products from selected commodities.

At this writing, work on Part I has been completed. This paper is a description of the test system and the theoretical concerns addressed in its design, and the analytical protocols developed for combustion product identification.

Theoretical Constraints

Physical conditions surrounding a tank car fire had to be established before an apparatus could be designed. Therefore, the scenario, illustrated in Figure I, was employed as a standard for experimental design purposes. Under this situation, a tank car is assumed to have a single breach in the shell. The product is assumed to be at ambient temperature in liquid form. Conditions surrounding ignition were not considered and the product is assumed to be on fire.

Additionally, several environmental assumptions were made: 1) that all burns would occur in a normal air atmosphere; 2) environmental pressure would remain around one atmosphere and expected deviations from this would have little effect on the burning system; 3) the relative humidity would range from between 0 to 100 percent; and 4) burning conditions would range from a minimum of air required to support combustion to a condition of unlimited supply.

System Dynamics

It is assumed that exhaust gassing and influent air flow occur through the same opening. Because of this flow pattern, it is assumed that a dynamic equilibrium will be reached between influent air flow, product volatilization rate, total heat released from combustion, and exhaust gassing.

The size of the breach in the tank car shell would serve to regulate the volume of air flow and exhaust gassing withing the system. The maximum partial pressure of oxygen (PO_2) available would be 159.22 mmHg or 20.95 percent (Weast, et. al., 1980). This would correspond to an infinite supply of normal air. In the minimum condition, PO_2 would approach the lower limit of normal air necessary to support combustion.

Heat energy transferred to the tank car shell shown in Figure I will radiate back into the liquid phase material. This will increase the volatilization rate. Assuming the compound to be in excess, oxygen pressure will dictate the rate of product consumption. As more product volatilizes, more oxygen would be required to sustain combustion. Therefore, when the upper oxygen limits are reached, total energy release from the combustion reaction would also be maximized. Under these conditions, the system is at equilibrium.

The interdependence of these factors in a closed system can be represented stochiometrically as:

$$\left(C_\alpha H_\beta O_\gamma\right) + \left(\alpha + \frac{\beta}{4} - \frac{\gamma}{2}\right) O_2 \longrightarrow \alpha CO_2 + \frac{\beta}{2} H_2O \qquad \Delta H \qquad \text{(Equation 1)}$$

for the complete combustion of an organic compound (Krause and Gann, 1980).

If one takes the molar proportion of oxygen in a standard atmosphere to be .2095 moles/23 liters (Weast, et. al., 1980), and sets

(Equation 2)

$$N = \frac{.2095}{\alpha + \frac{\beta}{4} - \frac{\gamma}{2}}$$

Where N is the number of moles of product which can react completely with .2095 moles of O_2.

the combustion equation then becomes:

$$N\left(C_{\alpha}H_{\beta}O_{\gamma}\right) + .2095\,O_2 \longrightarrow N\alpha CO_2 + N\frac{\beta}{2}H_2O \qquad N\Delta H \qquad \text{(Equation 3)}$$

for cases where O_2 is the limiting reagent.

The theoretical maximum oxygen concentration is constrained by the normal atmospheric gas mixture. However, $O_{2(min)}$ required to support combustion is chemically dependent. During an actual tank car fire, the O_2 available to the reaction will range between $O_{2(max)}$ to $O_{2(min)}$ as a function of the volumetric flow rate.

Based on the constraints derived from our scenario, the furnace design had to allow direct measurement or control of the four key variables, oxygen concentration, system temperature, flow velocity, and sample temperature.

Furnace Design

The combustion chamber, illustrated in Figure II consists of a 0.64 cm thick stainless steel cylinder measuring 20. cm in diameter and 61. cm in length. A demountable stainless steel funnel was affixed to the top which terminates with a 3.5 cm I.D. A door located approximately 15 cm from the base allows access to the sample. The sample rests in an aluminum block which is fitted with a heating coil to allow control of sample temperature prior to ignition. A nichrome igniter runs through the block to the sample well. Thermocouples are placed at the block, above the sample, and on the funnel. The thermocouple above the sample functions only to record the duration of the sample burn.

Air flow is introduced at the base of the cylinder through a perforated, coiled, copper tube into a 0.64 cm thick bed of glass beads. This ensures a uniform flow velocity through the cylinder.

To reduce the potential for condensation of combustion products on the funnel, heating panels were applied.

Determination Of Burn Rate

Prior to sample burning, the filter which is used to collect soot, is placed in the filter holder. The filter holder and the funnel at the top of the combustion chamber are then heated to $160^\circ \pm 5^\circ$ C. Once this temperature is reached, a Tenax tube, a charcoal tube, and a vacuum pump are placed in series respectively after the filter, by the use of Swage-lok-type fittings. The flow rate of oxygen through the chamber is maintained at 10 liters per minute throughout the burn period. The percentage of oxygen used can be quantitatively decreased from approximately 20 percent to 0 percent by adding the required percentage of nitrogen to compressed air. (The compressed air is dried by being passed through a cylinder of Drierite before reaching the chamber.)

A 7.0 ml aliquot of the sample is placed into a platinum crucible, the crucible placed in the sample block holder inside of the chamber, and the door to the chamber closed. (The sample block holder is maintained at 25°C for all samples except N-butanol (35°C), styrene (34°C), and xylene (34°C). The higher temperatures are required for the ignition of these three samples.) A nichrome wire above the sample is used to ignite the sample. Once the sample ignites, the sampling pump is turned on and left on until the flame goes out. (The flow rate of the pump is set such that iso-kinetic sampling through the sample pores is achieved.)

The sample ignition, burning, and end-of-burn are monitored by an iron/constantan thermocouple positioned directly above the crucible. The thermocouple is connnected to a Fisher Recordal Series 5000 recorder giving an output in millivolts which can be converted to degrees C. The recorder is calibrated to run at 2.5 cm/min, thus, the burning can be timed and recorded as a burn rate in units of grams of sample burned per minute. (Although the burn rate is actually dependent on the size and shape of the crucible, using the same crucible for each burn allows a comparison of the values obtained for the various samples.)

The burn rates were measured using 20 percent, 15 percent, and 10 percent oxygen. When using less than 20 percent oxygen, the entire chamber is flushed with the air/nitrogen mixture for two minutes prior to introduction of the sample.

Sampling

The products of combustion are sampled through a port at the top of the open-burn chamber, as shown in Figure II. The sampling train is shown in Figure III. The inlet to the sampling train is a downward-facing teflon-coated stainless steel tube of 0.635 cm O.D. The temperature of the tube and filter housing are maintained at approximately 160°C., using a resistive heater. The stainless steel filter holder contains a 37 mm diameter glass-fiber filter (Gelman GFF/A. Gelman Sciences Inc., Ann Arbor, Michigan) supported by a stainless steel screen. Particles larger than approximately

0.1. microns are removed with 99+ percent efficiency by the filter. Prior to and subsequent to sampling, the filter is brought to constant relative humidity in a 50 percent R.H. chamber, and weighted on a digital electronic micro balance. The mass of particulate matter collected is obtained from the difference in weights.

Vapors are collected in sorbant tubes attached in series between the filter and the sampling pump. Higher molecular weight gases and vapors not deposited on the filter are collected in a tube containing 0.155 ± 0.005g Tenax-GC, 60/80 mesh (Supelco Inc., Bellefonte, Pa.) This sorbant is recommended by the U.S. Environmental Protection Agency for collection of species with moderate molecular weights. The tubes are prepared in a laboratory. More volatile vapors are collected on charcoal. The use of tubes containing activated charcoal is the standard National Institute for Occupational Safety and Health procedure for sampling of low to mid-molecular weight organic compunds. The charcoal tubes were obtained commercially (SKC, Inc., Appomatox, Va.) and meet the NIOSH requirements for such sampling tubes.

A carbon-vane vacuum pump is used to draw the sample through the train. A needle valve was used to regulate the flow, which is measured with a precision flow meter prior to connection of the sampling train to the port and immediately after sampling.

Flow Rates

Flow rate is an important parameter for several reasons. Aside from determining the length of time required to obtain sufficient sample (low concentration or flow requires longer time), the optimum range of flows for the charcoal tubes is from 50 to 200 ml/min, above which the potential for sample loss exists. Most important, however, is the effect of flow rate on the size distribution of particles sampled. In order to avoid biases in the sampling due to momentum of the particles, the flow rate of the sample must be adjusted such that its face velocity is the same as that of the stream being sampled. Under such conditions, the system is "iso-kinetic" with respect to particles and the sample free from size bias.

In the present system, iso-kinetic sampling is obtained by adjusting the flow of the sample stream. Given an inlet air flow of 10.0 liters per minute, the exit tube diameter (I.D.) of 3.5 cm and the sample probe diameter of 0.32 cm, the flow rate of the sample stream is calculated from:

(Equation 4)

$$\text{FLOW RATE} = \frac{10{,}000\ ^{\text{ml}}\!/_{\text{min.}} \left(0.079\ \text{cm}^2 \right)}{9.6\ \text{cm}^2} = 82.29\ ^{\text{ml}}\!/_{\text{min.}}$$

The total volume sampled, used in the calculation of concentration, was obtained by multiplying the flow rate by the length of time the sampler was on.

Sample Preparation Procedure

Filters

The filters used for soot collection are 37 mm glass fiber filters (Gelman Instrument Company, Ann Arbor, Michigan). Prior to sample collection, the filters are dried to constant minimum weight in an oven at 110°C for a period of at least 6.6 hours. The filters are then placed in a desiccator, at 50 percent relative humidity for at least 45 hours. After this period of time the filters obtain a constant weight at 50 percent relative humidity and are ready for use. (The desiccator was maintained at a constant humidity by use of an aqeous solution of sulfuric acid.) A Perkin Elmer (Perkin Elmer, Norwalk, Conn.) auto balance model AD-2 is employed to determine the weight changes of the filters.

The filter is divided into sections for subsequent analysis. Two portions are analyzed using an F&M Model 102 CHN analyzer (F&M, Inc., Evendale, Pa.). One of these portions is analyzed "as is" to give the total carbon content of the filter; the other is heated to 35°C for 30 minutes to drive off volatile organics. This latter sample is analyzed for the elemental carbon content. The difference between the two carbon masses obtained gives the organic content of the soot on the filter. The remainder of the filter is subjected to the extraction procedure below.

Tenax

The 60/80 Mesh Tenax GC used to collect the higher molecular weight organic compounds, is purified by soxletic extraction (Drost, et. al., 1982). The Tenax is first extracted for 12 hours using methanol as the solvent and then reextracted with N-pentane for 12 hours. A portion of glass wool is placed on top of the Tenax in the extraction thimble and simultaneously extracted. Following the extractions, the Tenax and glass wool are dried in an oven at 110°C for 5 hours, and stored separately in glass jars with aluminum lined lids. The glass tubes which hold the Tenax for sample collection are 0.64 cm O.D., 0.32 cm I.D., and approximately 15 cm in length. The tubes and the GC end caps used to seal those tubes (Alltech Associates, Arlington Heights, Ill.) are washed thoroughly with soap and tap water, rinsed with tap water, and then rinsed with distilled/deionized water. The tubes are dried in an oven at 110°C and the caps are air-dried. The tubes are then packed with Tenax and plugged at the ends with extracted glass wool. The bed length of the Tenax in the tube is approximately 11.5 cm and the weight of Tenax added is 0.155 ± 0.005 grams. After packing, the tubes are degassed at 275°C for one hour using helium at a flow rate of 10 ml/min. Once cooled, the tubes are capped with the GC end caps, stored over Drierite and refrigerated at 4°C until immediately prior to use.

Filter and Tenax Extraction Procedure

The Tenax or the portion of the filter and blanks for control to be analyzed using GC/MS and GC/FID are micro Soxhlet extracted first with chloroform for four hours, then with cyclohexane for four hours. The extract is then reduced to a volume of 1 ml in a graduated Kuderna-Danish evaporative concentrator. The concentrated extract is then transferred into a vile using a syringe. If the desorbed sample is not to be analyzed immediately, it is to be refrigerated. Samples are analyzed within two days of extraction to avoid quantitative errors.

Analysis of Extracts

The extracts from the filters and Tenax tubes are analyzed under similar conditions as shown in Table 1. Extracts of the charcoal tubes are chromatigraphed under similar conditions except for a lower starting temperature (35°C) due to the lower boiling points of the species collected on charcoal. Two different detectors are used to identify and quantitate the species present. A flame ionization detector, calibrated against injections of normal hydrocarbon standards of known concentration, is used to determine quantitative levels of each compound. A mass spectrometer is used to identify compounds by comparison of their fragmentation patterns with the known fragmentation patterns of over 50,000 organic compounds. Some subjectivity is required in spectral interpretation since the computer program written to do this search gives several possible species (and relative probabilities). In order to relate the two analyses, identical matched columns (2 meter glass, SP 2250 on 100/200 mesh Supelcoport) were obtained from the manufacturers (Supelco, Inc., Bellefonte, Pa.) for the two chromatigraphic systems. The GC/SID used is a Perkin Elmer model sigma 3 B with a Perkin Elmer model sigma 15 data station. The GC/MS is a Hewlett Packard Model 5840 A data processor (Hewlett Packard, Palo Alto, Ca.) linked to a Hewlett Packard Model 5985 spectrometer and chromatograph.

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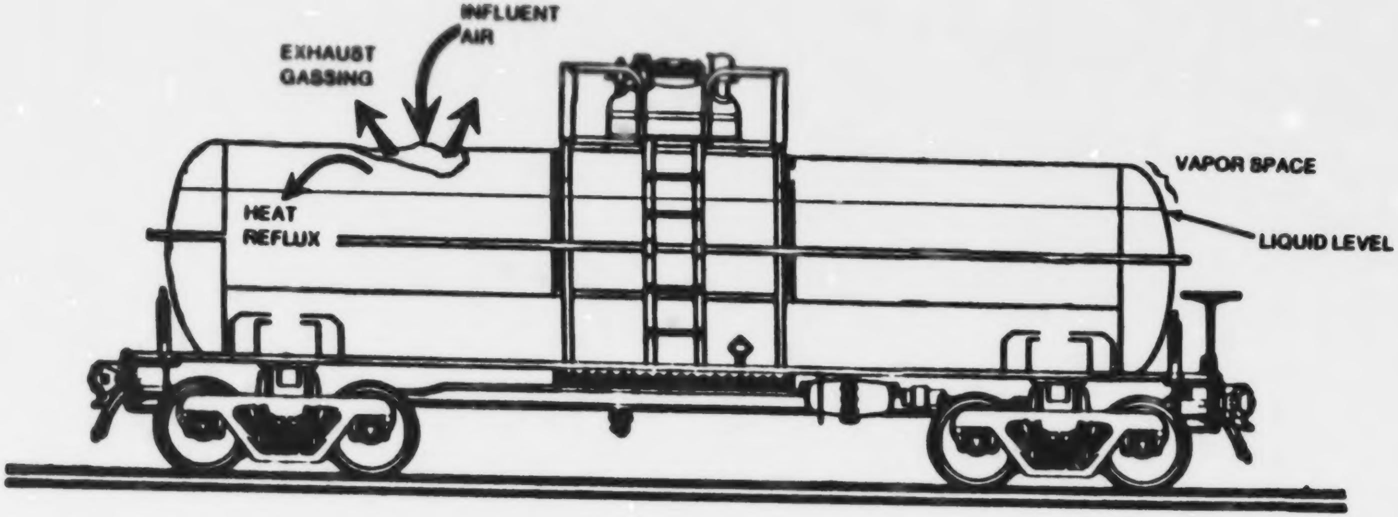
Table 1

Gas Chromatigraphic Conditions

Initial Temperature	40.°C
Initial Time	5.0 minutes
Ramp Rate	10.°C per minute
Final Temperature	250°C
Final Time Held	10. minutes
Inlet Temperature	270°C
Outlet Temperature (detector)	270°C

FIGURE I

Tank Car Scenario


INFLUENT AIR
EXHAUST GASSING
HEAT REFLUX
VAPOR SPACE
LIQUID LEVEL

Environmental Conditions

PRESSURE - 760 TORR

TEMPERATURE - 25°C

PO_2 - 159.2 TORR

RELATIVE HUMIDITY - 0 - 100%

FIGURE II

Furnace Design

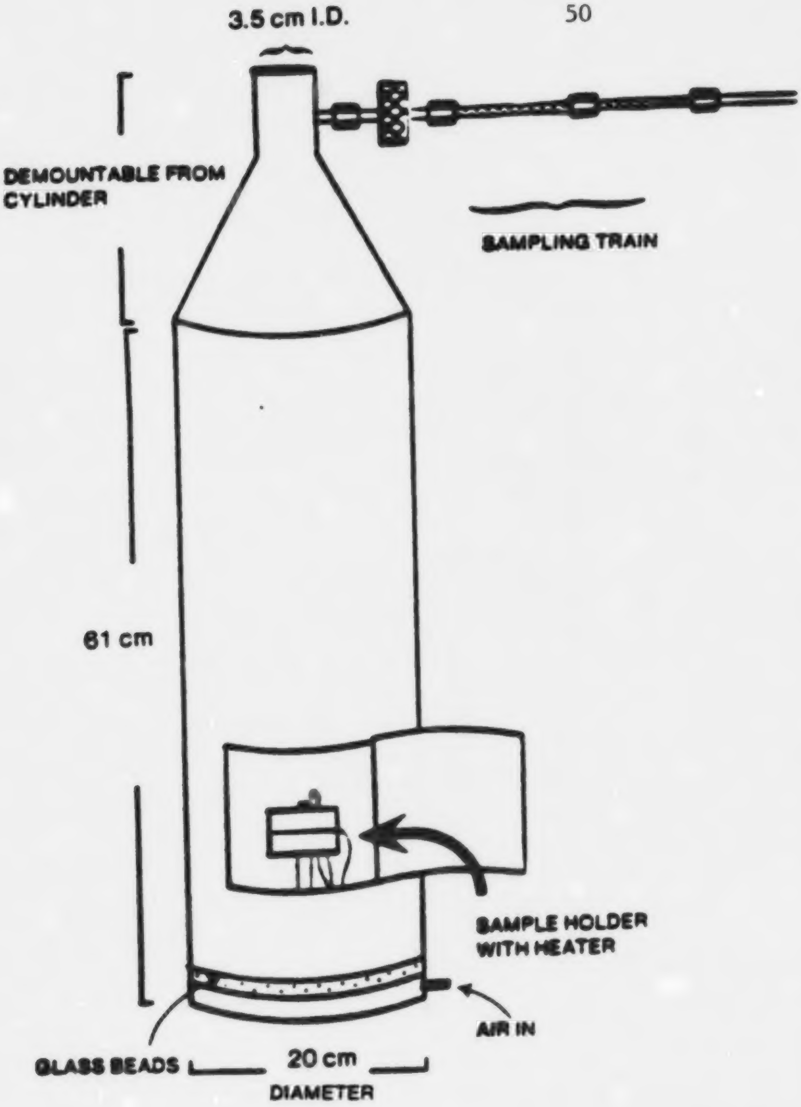
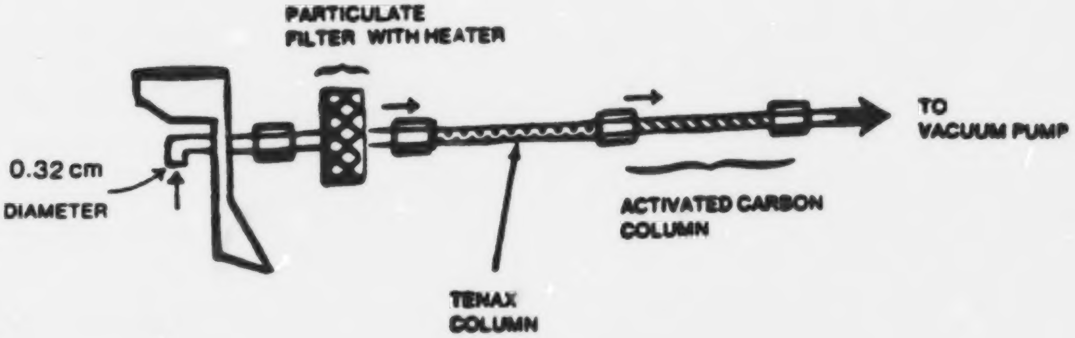

3.5 cm I.D.
DEMOUNTABLE FROM CYLINDER
SAMPLING TRAIN
61 cm
SAMPLE HOLDER WITH HEATER
AIR IN
GLASS BEADS
20 cm
DIAMETER

FIGURE III

Sampling Train Detail


PARTICULATE FILTER WITH HEATER
TO VACUUM PUMP
0.32 cm
DIAMETER
ACTIVATED CARBON COLUMN
TENAX COLUMN

FIRE AND EXPLOSION FROM FAILURE OF MOBILE TANKS

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1. INTRODUCTION

The development of industry and commerce and of the demands of society has led to the need for the transportation of a wide variety of materials many of which are of a hazardous nature. The means of transportation and the size of the load varies widely. So that at one end of the spectrum the movement of materials is continuous as in a pipeline while at the other extreme, small bottles and phials are used for the delivery of discrete packages of materials. There are no grounds for discounting hazard on the basis of size alone.

The range of hazards is wide and it includes fire and explosion, asphyxiation, poisonning,corrosive attack and microbial activity (1). From the wide range of loads and of methods by which they are carried, attention will be directed in this paper to the hazard of fire and explosion from a method of transportation found in the "middle" of the size range. This has been referred to in the title as mobile tanks, by which is meant tank cars and tank trucks. This is not intended to even suggest that the fire and explosion hazards from drums of fuel and oil and from cylinders of liquefied and /or compressed gases are of no consequence.

1.1 Range of Materials Carried in Mobile Tanks

This range has increased significantly over the last 30 years. Materials are now carried in a state that would then have been considered hazardous or even impossible. In Table 1, some examples are set down of materials presently carried.

Table 1. Examples of materials carried in mobile tanks

MATERIAL	STATE	CONTAINER
Nitrogen	liquid	Insulated tank at atmospheric pressure; cryogenic fluid
Oxygen	"	
Hydrogen	"	"
Methane	"	"
Ethylene	"	"
Hydrogen	gas	Pressure vessel; compressed gas
Methane	"	"
Ammonia	liquid	Pressure vessel, liquefaction by pressure
Chlorine	"	"
Butane	"	"
Ethylene	"	"
LPG	"	"
Propane	"	"
Sulphur dioxide	"	"

MATERIAL	STATE	CONTAINER
Bitumen	Liquid	Tank at atmospheric pressure; contents at elevated temp.
Phosphorus	"	
Sodium	"	"
Sulphur	"	"
Particulate solids e.g. flour, sugar, cement	Solid	Tank at atmospheric temperature and pressure; contents removed by fluidisation
Gasoline	Liquid	Tank at atmospheric temperature and pressure
Kerosene	"	"
Caustic soda	"	"
Sulphuric acid	"	"
Aromatic hydrocarbons	"	"
Methyl chloroform	"	"
Trichlorethylene	"	"
Carbon tetrachloride	"	"

With many of these materials if containment is lost an immediate hazard is created. Of the ones that may be involved in fire and explosion a number of possibilities are listed in Table 2, which seeks to draw attention to the number of different events that may be produced involving mobile tanks.

Table 2. Involvement of tank contents in fires and explosions

MATERIAL	STATE G-gas L-liquid S-solid	FIRE P-pool T-in tank	EXPLOSION C-confined U-unconfined	OTHER HAZARD
Oxygen	G,L	-	-	Increases probability of ignition and combustion of other materials
Hydrogen	G,L	P,T	C	
Methane	G,L	P,T	C	
Butane LPG Propane	G,L	P,T	C,U	BLEVE, UVCE
Styrene	L	P,T	C	Self-heating to runaway
Phosphorus Sodium	L	P,T	C	Acid fumes from phosphorus and hydrogen evolution from sodium
Particulate solids	S	T	C	Smouldering ignition by static electrification

1.2 Mobility

All of the examples listed in Table 2, involve materials that are moved on both road and rail and are stored in large quantities in static tanks. The mobility factor is of importance in several ways that are listed briefly here.

(i) the proximity of areas of dense population becomes largely a matter of chance rather than design

(ii) the likelihood of rupture and spillage is markedly increased over that for static storage

(iii) segregation of different types of loads is not followed through in parking lots for trucks and in marshalling yards for tank cars. Loads that in loss of containment are incompatible, may be in close proximity

(iv) the speed at which vehicles travel varies but in normal operation is under the control of the driver (engineer). Under conditions where the system fails this may no longer obtain. Thus protection of tanks e.g. head-shields, corrugated barrier shields, require design to be adequate for conditions well outside the planned range. The velocity at which mobile tanks may be expected to encounter sharp objects or massive buffers against which they may be respectively either pierced or collapsed to rupture, may be other than according to normal design considerations.

(v) the probability of a mobile tank having a source of ignition in close proximity at the time of an accident is high. Ignition of flammable materials often occurs immediately rupture takes place and the flammable gas/vapour is released from containment.

1.3 Size of Tanks

As already suggested size alone offers a very incomplete basis for judgement of hazard. Shifted and shed loads of cylinders, drums and small tanks arise for consideration in the general matter of hazards from freight-carrying vehicles.

Tanks vary considerably in size according to the material carried and the service for which it will be employed. Thus tank trucks may have capacity in the range 8000 or even less up to 50,000L (tractor trailer). The weight carried in such atmospheric tanks varies with the density of the material carried.

Tank cars also vary in volume. "Jumbo" tank cars at 76,000L for moving gasoline are used widely. Larger ones at 89,000L are also used. The size of cars is limited by rail loading so that the contribution of a pressure vessel for compressed gas to the gross weight, is a matter of importance.

Because of the wide variety of tank sizes, of materials and of their densities and state, detailed reference to magnitude of hazards will be considered below in terms of the behaviour of loads of 30 tonnes. For some effects the result is directly proportional to weight, but this is not universally true. It will therefore be necessary to comment on this effect where appropriate.

1.4 Sources of Ignition

In discussing hazards due to fires and explosions there is a tacit assumption that ignition has already occurred. Exploration of the initiation of a phenomenon therefore does not arise in the present context. However some brief general observations will be made here.

(i) sources of ignition are fairly regarded as ubiquitous

(ii) reduction and minimisation of the number of sources of ignition is a reasonable aim. In practical systems the elimination of all sources of ignition is virtually impossible

(iii) in crash situation involving tanks and in loading and unloading tanks containing flammables the following sources of ignition may be present:

(a) hot surfaces
(b) incendive sparks from grinding
(c) static electrification
(d) power discharges
(e) adiabatic heating due to compression
(f) chemical reaction (other than combustion)

2. RELEASES FROM TANKS

Attention has been directed in Tables 1 and 2 to the fact that gas, vapours, liquids and solids may be involved in fires and explosions in tanks. Fires may take place within the containment of a broken tank or outside the tank with the flame burning in the vicinity of a port or of a breach in the tank. In this latter case the flammable material may be fed to the flame either by reason of the fact that originally it was pressurised or there may be feed back of thermal radiation, as in a pool fire, to vaporise more fuel from remaining liquid.

The other simple system is that whereby liquid escapes from a tank at atmospheric temperature and pressure because containment has been lost. The hole may be due to a variety of reasons e.g.

corrosion
broken fittings
failed fittings
piercing or fracture in collision

It is likely under these circumstances that there will be a gravity-feed of flammable liquid to a pool fire

The array of mechanisms by which flammable materials are released from tanks is extensive. Some pertinent aspects will be explored here.

2.1 Modes of tank failure

2.1.1 Corrosion. Corrosion may be simple or conjoint and the electrochemical agent may be within or without the tank. Stress and fatigue cracking and hydrogen or caustic embrittlement may be active. The action of chlorion in pitting corrosion is a further cause of failure.

Failure by these mechanisms and by stress raisers arising from impact bear less than direct relation to the original design specification. This should not be the case for tank failure arising from embrittlement due to low temperatures.

Loss of containment may also arise from the tank fittings i.e. valves, gauges etc. Loss of fittings, failure of fittings and release from relief valves by reason either of jammimg open or of allowing passage of liquid or gas in non-designed orientations.

These modes of failure are often active in the case of a good tank that is weakened and fails due to overpressurisation in its weake ned condition, i.e. the overpressurisation is normal working pressure. Thus overfilling and heat, normal loading and fire and excessive pressurisation at loading may all bring about failure.

If the material in the tank can react exothermically e.g. polymerise, decompose, it may self-heat to runaway. Catastrophic tank failure may well result. The effects may include explosion, missiles, fire of the residual material and toxic fumes from the reaction.

2.2 Expulsion of Material from the Tank

If a tank fails compressed gas contained within it will escape to produce a momentum jet. If liquid at atmospheric pressure is within the tank, there will be a flow until the liquid level has fallen below the breach. When the liquid is cryogenic the same situation applies although there may be some two-phase flow until the shell cools. Collection of the released cryogenic liquid on the ground is subject to a cooling down period during which 'flash' evaporation occurs. The nature of external fires is influenced by this latter step.

When the contained liquid is gas held under pressure e.g. propane, two-phase flow will occur at the breach. This may be important in determining the rate at which the material returns to the gas phase and also the degree of entrainment and mixing with air. The likelihood of an unconfined vapour cloud explosion (UVCE) or of a boiling liquid expanding vapour explosion (BLEVE) depends on these aspects. The mode of release is also likely to determine the temperature of the resulting gas/vapour and therefore whether it becomes a heavy or light vapour cloud. This may be important in determining either the type of fire e.g.methane from LNG or the toxic hazard e.g. ammonia from compressed storage.

3. HAZARDS

Considerations in this paper are confined to fire and explosion. It is recognised, however, that non-ignition of a release from a tank may cause asphyxiation in relatively close proximity to the tank and also acute toxicological effects. Although the topic will not be explored here it is necessary to examine the likely effects of products particularly from fires. These are usually toxic to some degree (e.g. on account of carbon monoxide) and the dispersion of these products provides a measure of the hazard. The thermal lift of the products is normally great enough to ensure safety in open country but this aid to dispersion may be interrupted in urban areas.

3.1 Fires

Several types of fires may be generated from flammable materials that are transported in tanks. Their occurrence depends on the magnitude of the release, upon the material contained and the exact conditions of containment. A brief summary of these aspects is given below.

3.1.1 Turbulent diffusion flame. These are generated from gas stored under pressure. Such a flame will also be generated from gases containing liquid droplets. If the hole is large or the tank bursts the likelihood arises of either massive gas release or two phase flow that will be combusted at some distance from the tank in the form of a fireball, a BLEVE or a UVCE.

3.1.2 Tank Fires. The contained material may burn in a diffusion flame at the free surface arising from the holed tank. Such circumstances occur with flammable liquids in atmospheric tanks.

The tank and material combination of this type may produce a running fire. In this case the liquid not only burns at the tank but on the surface of the streams from the tank. This type of fire occurs when tanks collapse and usually when they are holed at low level.

3.1.3 Pool Fires. Spillage of flammable liquid that collects on the surface beneath, provides a source for a pool fire. If the liquid is cryogenic there is an added step (and delay) while the substrate is cooled down; during this period 'flash' evaporation occurs. When the substrate has been cooled, the liquid is likely to be consumed at a steady regression rate.

In all of these fires the size and temperature (T) of the flame are of importance. Radiant flux depends upon T^4 and a guide to flame size for liquids is afforded by taking flame height as equal to twice the diameter of the exposed surface (2). The effect of wind in bending the flame and the proximity of other flames as it may influence flame-merging define the magnitude of the hazard. In the case of fires from tanks of compressed gas the original pressure and the feed back of thermal radiation are important in determining the size of the flame and hence the thermal radiation generated.

3.1.4 Fireballs. These occur when the gas cloud is above the upper flammable limit and the uplift of the thermal gradient is too great to allow the normal processes of a diffusion burning to take place. Fireballs are often generated from fires of liquid hydrocarbons; one of the outstanding examples is that provided by combustion of liquid hydrogen when a succession of fireballs breaks away from the flame plume.

The diameter of the fireball (which depends on mass) and its direction determine the magnitude of the hazard as does radiant flux which depends upon both calorific value, emissivity, attenuation within the fireball and, to a lesser extent, by the surrounding atmosphere. For a hydrocarbon of calorific value 46.5 MJ kg^{-1} the energy release per unit surface area is

2516 KW m^{-2} using $d = 4.1\ m^{\frac{1}{3}}$
d - equivalent spherical diameter (m)
m - mass (kg)

The duration t (s) may be calculated from:

$$t = 0.35m^{\frac{1}{3}}$$

when account is taken of the attenuation factors it has been suggested that the net emissive flux is 500KW m^{-2} (3).

3.2 Explosions

These are of two types viz confined and unconfined. The first type of confined is related to inspection, maintenance and control. It is brought about by failure of the tank when it is subjected to a pressure in excess of that which it is able to contain. This situation may arise from overloading (lack of control) or in tanks that have been subjected to corrosion or conjoint corrosion (inspection and maintenance). While overloading may produce failure immediately, the failure may be delayed until the effects of exposure to strong sunlight have caused expansion to take place.

The effects of such failures that are usually ductile rather than brittle, include the following:

blast waves
missiles that may include parts of the traction unit
fire
rocketting of large parts of the tank

3.2.1 Confined Explosions. Aside from the situations outlined in 3.2 confined explosions can arise from sudden generation of energy within the tank. The most usual process involved is combustion. To avoid this situation tanks are normally operated with a residue left within the tank after loading. However in the case of tanks of liquid the induction of air into the ullage space of the tank is a live possibility. The introduction of a source of ignition into such a flammable mixture will generate pressures 8 to 10 times the original value. The energy generated by the combustion reaction will be partitioned between a blast wave and missiles, depending upon the nature and state of the tank material and the characteristics of the combustion.

It is not always appreciated that a tank of pressurised gas/ or vapour may progress into a second phase of combustion as the initial diffusion flame external to the tank and stabilised at the breach, dies away when the pressure decreases to atmospheric; combustion can take place in a "reversed" system (4). In this situation air is drawn into the tank and a reversed flame persists inside the tank. Depending upon the geometry of the situation and upon the flammable gas, this state of affairs can persist until the bulk of the tank attains the composition of the lower limit of flammability. Explosion then takes place with a consequent pressure rise of about 5 times ambient.

Confined explosions may also occur from fast exothermic reactions arising from, for example decomposition or polymerisation. Organic peroxides provide an example of the first type when gaseous products of decomposition are produced and the reaction is strongly exothermic. Styrene exemplifies the second type; initiation may be by heat or by catalysts. In both cases as temperature rises runaway follows and the heat generated from the reaction raises the pressure by expansion of the contents of the tank.

3.2.2 Unconfined Explosions. Concern here is with BLEVE's and UVCE's. A BLEVE is usually associated with tanks that contain liquefied flammable gas. The usual precurser is for the tank to be engulfed in flame; sometimes it results from the impingement upon the upper part of the tank of a flame from a relief valve. If the point of the impingement is above the liquid level in the tank, cooling of the shell is absent and it will fail. Thereupon the vapour is released which produces a blast wave as does that portion of the vapour that is mixed with air. The remainder of the flammable vapour produces a fire ball that emits thermal radiation as discussed in 3.1.4.

If the release of flammable gas or vapour is rapidly mixed with air so that a large premixed cloud forms which then encounters a source of ignition a UVCE can be produced. The resultant blast wave causes extensive damage to buildings and to lighter plant. In the context in which this damage occurs it is not unusual for fires to result as a secondary effect from the blast wave.

In all of the explosions mentioned above attention has been drawn to the blast wave. Behind the blast wave air flows in the pressure field produced; this air flow is usually referred to as the windage and causes damage by both carrying missiles from the explosion and converting into missiles unsecured objects in the vicinity of the explosion. In addition to that period of time when local pressures are raised above ambient (positive duration) there is also a further damaging phenomenon when the pressure is reduced below ambient (negative duration). Damage patterns from confined and unconfined explosions of flammable gases and vapours are likely for these reasons, to be complex. It may also be noted that meteorological factors may extend the range of damage beyond that to be expected as for example in the case of the propane release and subsequent UVCE at Port Hudson Missouri (5).

4.QUANTIFICATION OF SOME EFFECTS

4.1 Available Energy

In failing tanks there is often energy due to pressurisation; it is always present for compressed gases. It is present when tanks are overfilled with liquids and are subsequently pressurised. The energy stored in gas of original pressurem P_1 and volume V_1 when released to pressure P_2 where it occupies a valume V_2 is,

$$\frac{P_1V_1 - P_2V_2}{1 - \gamma}$$

where γ is the ratio of the specific heat at constant pressure to that at constant volume.

Using the same notation, the energy in stored liquids is given by

$$\frac{V}{2K}\ (P_1^{\,2} - P_2^{\,2})$$

where K is the bulk modulus of the liquid.

When the flammable gas or vapour has been released it can mix with air and enter into combustion. The available energy can be expressed on a per unit basis (30 tonnes here) and, assuming complete combustion, it may be derived from the heat of combustion. The quantity of energy expressed in TJ is indicative of what may happen in the system in the context of thermal radiation (for fires) or blast energy (for explosions). In the former case an estimate of the rate of consumption of the fuel can be incorporated to give a value for radiant flux (kW m^{-2}). In the second case it is often useful to express the value as TNT equivalent. Some values for 30 tonnes of fuel are given in Table 3

Table 3. Energy available from 30 tonnes of hydrocarbon; quantities expressed as TNT equivalents

MATERIAL	TJ/30 TONNES	TNT EQUIVALENT (TONNES)
Methane	1.7	340
Propane	1.5	310
Pentane	1.47	300

The values in Table 3 assume that the total energy from the hydrocarbon is available. In the event of a UVCE involving propane this may be as low as 1% but it could be as high as 20%. However these values reinforce the idea that large stores of energy are transported in tanks and that their maximum effect in fire and explosion is catastrophic. As the load increases the available energy increases proportionally.

4.2 The Unloaded Tank Situation

In order to gain some insight into this situation the postulate is made that a tank containing propane is emptied and that the space is filled with a propane/air mixture of composition equal to the lower limit of flammability (i.e. 2.12%(v/v)in air). This is the situation related either to draining down with ingress of air or, less closely, to the reversed flame system. The results for tanks of 10, 30 and 60 tonnes are given in Table 4. Also included are the distance for breakage of windows based on the TNT equivalents calculated and assuming that the energy is released entirely in a blast wave. Due to the imprecision of information relating to the breakage of window glass two values of scaled distance (S.D.) viz 40m $kg^{\frac{1}{3}}$ and 80kg $m^{\frac{1}{3}}$ have been used; these values are for the distance for 50% breakage. This effect does not increase directly with increasing load.

Table 4. TNT equivalent of unloaded propane tanks filled with lower limit mixture and the corresponding radius for window breakage.

SIZE OF TANK (tonnes)	TNT EQUIVALENT (kg)	APPROX. DISTANCE FOR 50% WINDOW BREAKAGE(m)	
		S.D. 40	S.D. 80
10	8	80	160
30	16	100	200
60	24	116	222

If a tank of propane (unit 30 tonnes) is emptied to 2% of its load the TNT equivalent of the residue is 6 tonnes calculated on the same basis as in Table 3. The energy in the compressed gas will be equivalent to 20kg TNT. Thus in the case of propane which can be liquefied at relatively low pressures, the energy in the compressed gas is small compared with the energy available by combustion of the hydrocarbon.

4.3 Thermal Radiation From Fireballs

It has been noted already that fireballs can occur in a fire or as part of a BLEVE. In both cases the hazard which may be severe (6) from the fireball is produced from the thermal radiation.

The values given (3) in Table 5 are based on the assumption of a radiant flux of 0.5MW m^{-2} at the surface of the fireball. For a fireball of diameter d(m) and with its bottom at height h(m) above the ground, the radiation fluxes have been computed for various valuesof r(m) i.e.ranges measured directly from below the centre of the fireball.

Table 5. Radiation flux density to the ground at range r/d from a fireball of diameter d at clearance h/d above the ground.

	Radiant flux (kW m^{-2})				
r/d	0.25	0.5	1.0	2.0	3.0
h/d					
0.25	1630	216	11	2.1	0.76
0.5	1333	173	25	5.8	0.85
1.0	839	133	38	7.3	2.47
1.5	625	110	35	4.2	3.75
2.0	561	95	34	4.2	4.06

The flux immediately beneath the fireball decreases with increasing values of h, but at some distance removed flux increases to a maximum and then decreases. The radiation flux for the pain threshold is usually taken as 4.7kW m^{-2} while the value for ignition of wood and roofing felt is 12.5kW m^{-2}

4.4 Effects from the Failure of a Spherical Propane Tank containing 30 tonnes of Propane.

It will be assumed that the following obtain:

Mass of propane	30 tonnes
Storage pressure	20 bar gauge
Ambient temperature	300K
Diameter of storage sphere	5m

Pressure distribution due to the bursting vessel (based on (7))

Radii (m)	2.5	4.7	7.5	18.7	30	37	47
Overpressure (kN m^{-2})	310	178	112	38	21	16	11

If a UVCE results and the generous 28% estimate due to Maurer (8) is used the radial ranges for overpressure employing the models of Gugan (9) and Clancey (10) are given below.

OVERPRESSURE (kN m^{-2})	RADIAL RANGE (m) Gugan	Clancey
50	49	61
42	68	83
24	99	114
15.9	130	147
6.9	228	268
2.0	519	703
1.0	825	1214

A general rule relating to the range of missiles is that it is limited to an overpressure of 2kN m^{-2} (11)

If the release of propane results in a BLEVE the following list of features is indicative of the effects of the event:

Burning time	10.9s
Diameter	127m
Average rate of energy release (based on 50% involved in non-percussive combustion)	75.6 GW
Radiant flux (neglecting attenuation)	2268kW m^{-2}

On the basis of Table 5, this suggests that if the fireball clears the ground by 50m those within a range of 150m would be severely burned and those out to 200m will experience pain.

The aspect of rocketting has not been examined here due to the large variety of scenarios. The results of an actual incident (6) where somewhat less fuel was involved than the 30 tonnes considered here, is a good indication of typical values for the range of large sections of tank shell.

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CONTROL OF THE VAPOR HAZARD FROM WATER REACTIVE VOLATILE HAZARDOUS MATERIALS BY FOAM

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INTRODUCTION

Water based foams have been used extensively for the control of the vapor hazard of spilled volatile flammable hydrocarbons. The ability of a foam to blanket such materials and prevent ignition is well recognized. It is a factor in the UL listing of foam systems[1] and a consideration in the NFPA standards on foam, 11 and 11A.

The capabilities of foam to mitigate the vapor hazard of the volatile hydrocarbons has led to the investigation of the capabilities for a broad range of other volatile materials. Two survey studies, one by the U.S. Coast Guard[2] and a second by the USEPA[3], have been conducted to review the available data. These two reports contain an extensive bibliography on the known technology. They deal almost exclusively, however, with the foam types readily available to and in wide use by the fire services.

These foam types have two major drawbacks to universal application against volatile chemical vapor hazards. They have limited application against water soluble organic chemicals and are rapidly destroyed by inorganic materials with strong acidic or basic characteristics. The needs of the water soluble organic (polar) compounds are adequately met by the newer polar solvent tolerant foams. The acidic/basic materials provide a more difficult problem.

The problem is twofold: first, the development of a foam system which is tolerant to pH extremes and second, the establishment of a market to support such products. It is clear that the fire services and other first response organizations will have difficulty justifying stockpiling a multiplicity of foam agents to address all possible spill situations and materials. The same is not true for chemical manufacturers and distributors who deal in specific commodities. In the last two years several programs have been conducted, directed to the evaluation of foam systems as a mechanism of vapor control for specific chemicals, with the ultimate objective the evolution of a foam system for the vapor mitigation of that chemical.

It is the purpose of this paper to review the results of those programs, to show the capabilities which exist for foam systems against certain chemical classes, to demonstrate the potential for in-plant systems and to provide some generalizations to be considered when contemplating the practicality of such foam systems.

COMMERCIAL FOAMS FOR ACIDIC AND/OR ALKALINE CHEMICALS

The earliest attempts to use foam with acidic or alkaline materials were directed to three specific commodities: ammonia, chlorine and sulfur trioxide. In these early tests[4-7] mixed results were obtained for these commodities using standard firefighting foams.

Typical responses for such foams against ammonia spills are shown in Figure 1. The high heat of solution between water and ammonia prevents low expansion

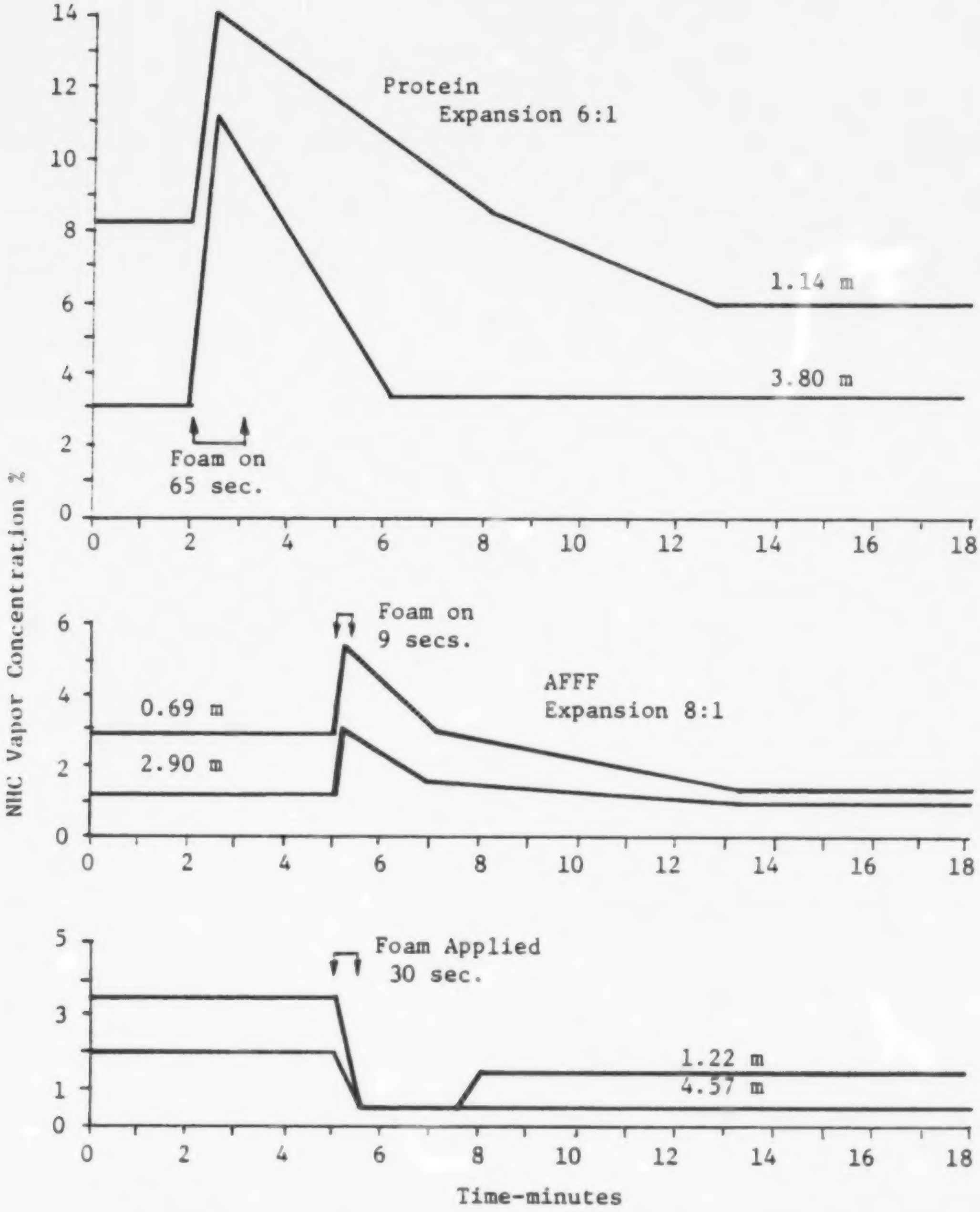


FIGURE 1. AMMONIA CONCENTRATION VS DISTANCE FOR THREE FOAM TYPES

foam from being effective. High expansion foam with its lower water content does reduce the downwind vapor concentration. The heat of solution assists by heating the released gas to a buoyant condition. The difference in concentration as a function of distance is felt to be due to this buoyancy effect.

With chlorine, standard foams are degraded fairly rapidly. In the process of degradation a layer is formed composed of ice and chlorine hydrate. This floats on the surface and ultimately reduces the rate of gas release from the liquid pool.

The data show that available fire fighting foams can have some beneficial results in combating the vapor hazard from ammonia and chlorine. There are limitations in the time and quantity of foam required to insure any benefits as well as with the magnitude of the benefits. Since both commodities have an extensive history of spills, there was impetus to provide foam chemistries which would be more effective than the standard materials. The recent commercialization of specific foam chemistries for ammonia and chlorine by National Foam and the delineation of the broad pH tolerance of MSA's Type V agent were initial steps in the evolution of special foam systems for water reactive hazardous chemicals.

WATER REACTIVE CHLORIDES

The availability of foams with an extended pH tolerance prompted experiments with the reactive metal chlorides, basically silicon and titanium tetrachloride, two materials in broad commercial use. Using MSA Type V foam a series of tests were conducted in cooperation with Teledyne Wah Chang to assess the ability of foam to control the vapor hazard from silicon tetrachloride.

These tests previously reported[8] showed that substantial reductions in the downwind chloride concentrations could be effected using either low or high expansion foam. Free spill chloride concentrations were reduced from 17,000 ppm to less than 200 ppm with almost complete elimination of a visible plume. Figures 2 and 3 are typical before and after conditions for these experiments.

In these tests it was observed that the foam-$SiCl_4$ interface was characterized by an encrustation of solids, mainly SiO_2, with HCl entrained in it. It was hypothesized that if HCl could be neutralized the effectiveness of the foam could be increased.

Laboratory tests using normal titres, such as the alkali metal hydroxides, did not support this condition. The reactivity between the acid and base was so severe that the effectiveness of the foam was actually degraded. The use of ammonium hydroxide seemed to avoid this problem. The crust formed was a combination of SiO_2 and NH_4Cl.

In large scale tests, using a foam made from a 14 V/O ammonia solution, the results were less than encouraging. The visible downwind plume was exaggerated over that of the free spill. Although the crust formed was basically SiO_2 and NH_4Cl as in the laboratory tests, the magnitude of the downwind plume was basis to rule the ammoniated foam a failure.

Following these tests another set were conducted in cooperation with Texas Instruments. In this case the reactive chloride was trichlorosilane. It posed a twofold hazard, the release of a toxic vapor and fire, since one of the products of hydrolysis of the liquid was hydrogen. A series of experiments similar to those with Wah Chang were conducted. The results with foam made with MSA Type V did not show the same degree of reduction of the downwind chloride concentration. This has been found to be relatable to the formation of a

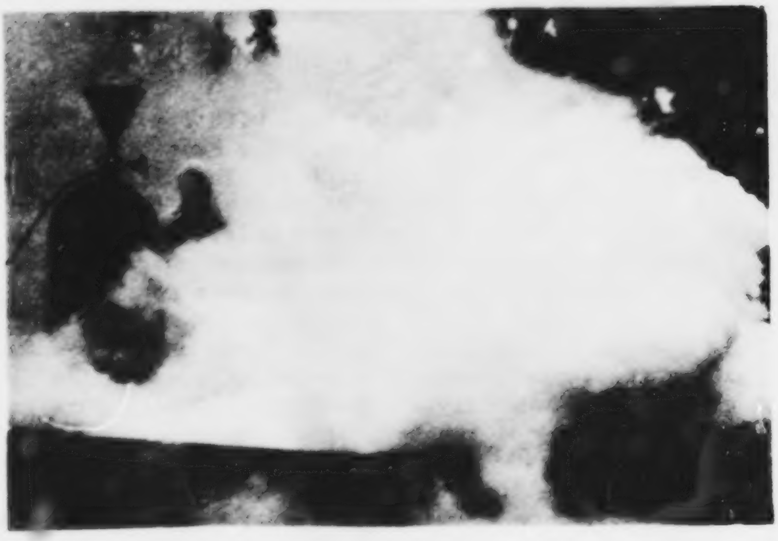


FIGURE 2. VAPOR CLOUD FROM $SiCl_4$ SPILL

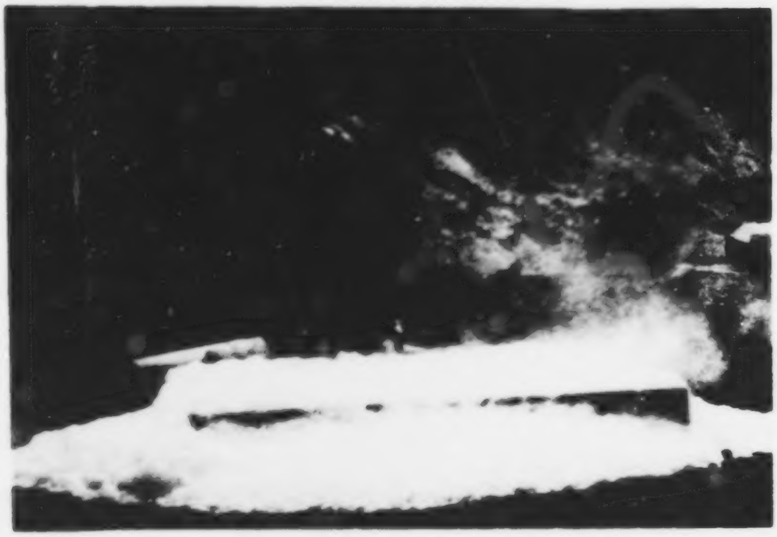


FIGURE 3. $SiCl_4$ SPILL WITH HIGH EXPANSION FOAM BLANKET IN PLACE

nonwater soluble gas, in this case hydrogen. This effect will be discussed for several commodities in a subsequent section.

Even though the mitigation of the vapor hazard was less than expected, the tests had some success. The foam did extinguish the hydrogen fires which occurred upon hydrolysis of the silane and allowed hydrolysis without burning.

In this sequence of tests, the ammoniated foam was given a second evaluation. As far as the magnitude of the downwind cloud was concerned, the results were no different than in the $SiCl_4$ experiments. Figures 4 and 5 are typical before and after conditions.

An additional observation was made, however. With unammoniated foam in both the Texas Instruments and Wah Chang tests, the reductions in chloride concentration were never sufficient to allow entry of the downwind area without breathing protection. When ammoniated foam was employed it was found that the visible downwind plume could be transited without breathing protection of any kind. This is due to the chloride being present as ammonium chloride rather than hydrogen chloride. Note that NH_4Cl does have a TLV but is not irritating to the breathing zone. The action of the ammoniated foam does not render the downwind zone completely safe but would allow the escape of anyone entrapped in the cloud.

One other study has been made on reactive chlorides, this one with thionyl chloride. These tests were sponsored by GTE Sylvania under U.S. Air Force aegis.[9] These tests were directed to a specific scenario, a small spill, occurring rapidly in a restricted area. This scenario lends itself to rapid flooding by foam. This inundates the spill and forms a layer through which all gaseous releases must pass.

In these tests the foam employed was specifically formulated to contain reactants for the species being released by hydrolysis of the thionyl chloride. SO_2 is the principal concern since it is only poorly soluble in water. The basic chemistry employed is given as follows:

$$SOCl_2+2H_2O+4CH_3COONH_4 \longrightarrow 4CH_3COOH+(NH_4)_2SO_3+2NH_4Cl$$

The success of these tests indicate that special formulations could be developed for a variety of chemicals. It should be noted that the system employed for the thionyl chloride is only adaptable to premixed foam solutions. Whether such capabilities could be developed into a system using a concentrate added to the water at the time of use remains to be determined.

ACRYLIC MODIFIED FOAMS

In 1971 efforts were made by MSA to develop a foam system effective against ammonia. Excellent results were obtained in the laboratory using a foam containing a water soluble acrylic polymer. The polymer reacted with the ammonia and gelled. A 30.5 cm (12 in.) layer of gelled foam suppressed the ammonia vapor below the odor threshold for up to 30 minutes.

The system was a practical failure, however. In field scale spills ammonia vapor could contaminate the air used to generate the foam. The result was gelling of the foam within the appliance.

In more recent work, sponsored by the U.S. Air Force, the acrylic modification of foams has been revived with good results. The Air Force in its search for a suitable spill control procedure for the hypergolic propellant materials hydrazine and nitrogen tetroxide conducted an investigation of vapor suppression techniques[10] in which foam was one of the mechanisms investigated.

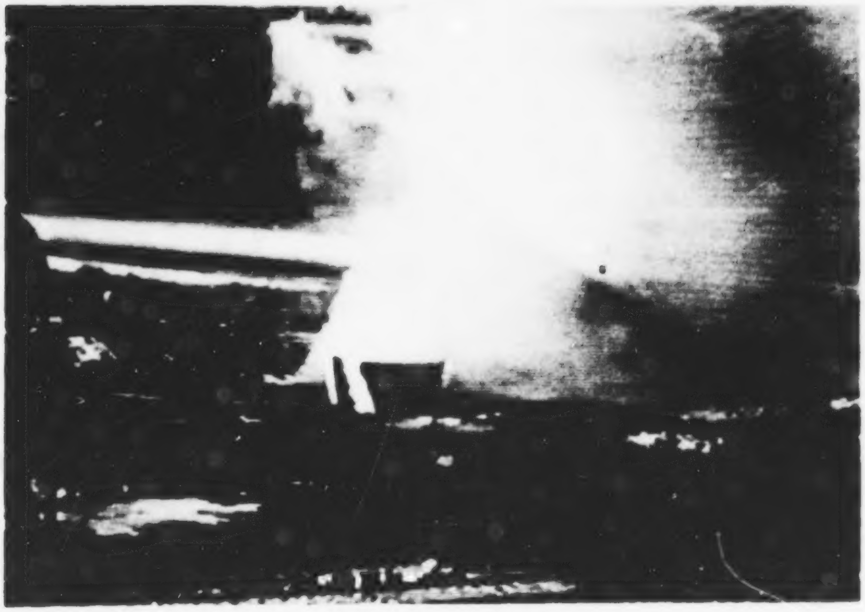


FIGURE 4. VAPOR CLOUD FROM SPILL OF Cl_3SiH

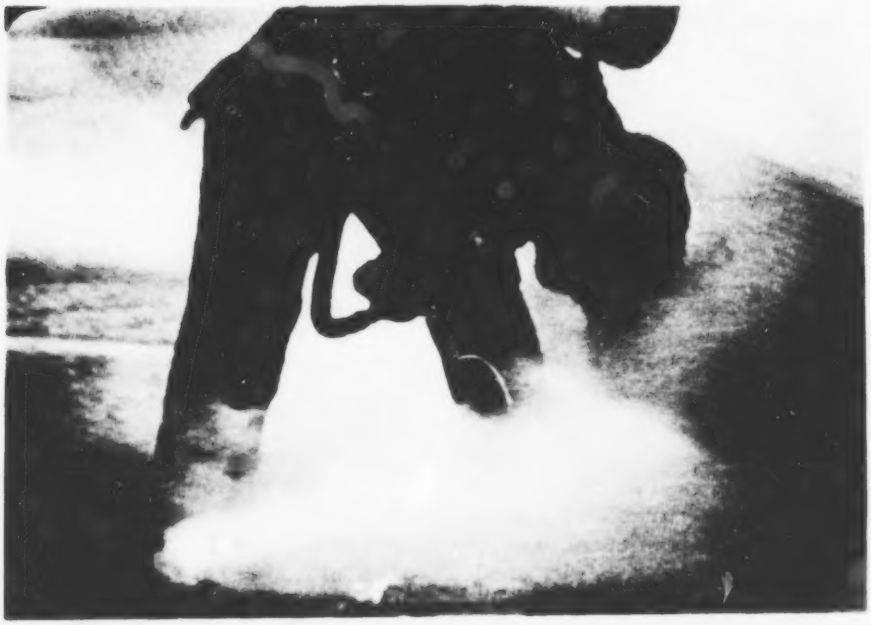


FIGURE 5. VAPOR RELEASE FROM Cl_3SiH SPILL AFTER THE APPLICATION OF AMMONIATED FOAM

Sufficient success was realized that an extensive development and test program was conducted.[11]

Since hydrazine is chemically similar to ammonia but with less volatility, the acrylic modified foam was one of the candidates evaluated. The results were very good. A foam chemistry was evolved which could limit the hydrazine concentration above the blanket to 0.2 ppm or less and maintain this concentration for an extended period.

The desire for a single foam chemistry effective against both the fuel (hydrazine) and the oxidizer (nitrogen tetroxide) led to the investigation of an acrylic foam system stable to the acidic nature of the oxidizer. To date no single system has been found but a second acrylic foam has been evolved with good vapor control capabilities against nitrogen tetroxide. The two foam chemistries are now in use onboard an Air Force spill response vehicle.[12]

The vapor reduction achieved by the acrylic foam when blanketing a pool of nitrogen tetroxide is shown in the sequence in Figure 6. The vapor release rate through the foam gives an NO_x vapor concentration above the blanket of about 100 ppm, split 90 ppm NO and 10 ppm NO_2.

LIMITATIONS IN VAPOR CONTROL

The best results with foam have been achieved with contained spills of materials which release a water soluble vapor. Where one of the gases being released is water insoluble it carries with it some percentage of any soluble gases. In the previously noted work with thionyl chloride, the difficulty of absorbing the SO_2 released rendered normal foams relatively ineffective. To a lesser extent the hydrogen from trichlorosilane and the NO from nitrogen tetroxide create the same effect.

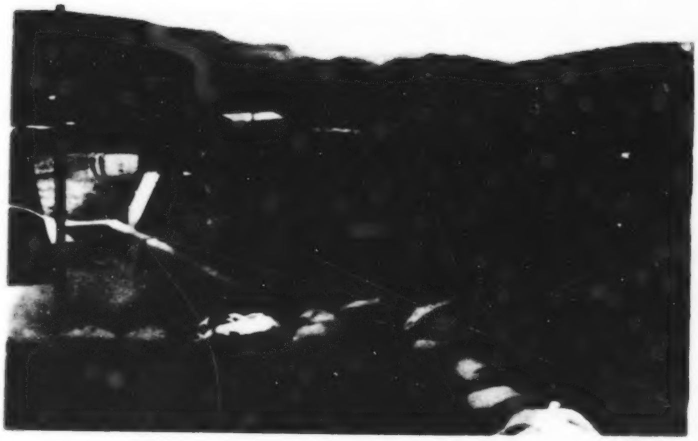
In contrast to contained spills, running or spreading spills are more difficult to control with foam. If the foam is fluid and spreads with the spill some degree of vapor mitigation can be achieved. High expansion foam provides the best effect. With N_2O_4, the release rate of NO_2 could always be kept below the visible range but the release of the nonwater soluble component of hydrolysis, NO, is relatively slow.

In tests conducted by Wyandotte Chemical with carbonyl chloride, $COCl_2$, less effective results were obtained. For this material the CO_2 released is a major component. Some degree of mitigation of the chlorine release was achieved in laboratory size tests of contained material. In larger tests, using running spills, foam proved to be totally ineffective.

DILUTION OF FOAM COVERED SPILLS

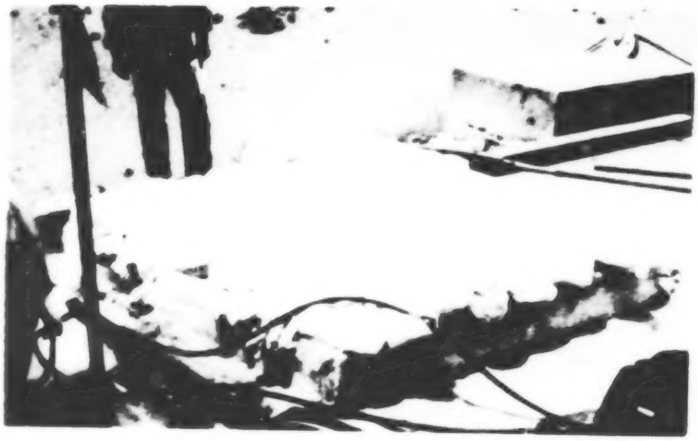
In many instances with water reactive or water soluble materials, dilution would be a useful mechanism of spill control. Certain chemicals are so reactive, however, that the direct addition of water exaggerates the vapor hazard. Figures 7 and 8 show the rigorous reaction of $SiCl_4$ and N_2O_4, respectively, upon the addition of water.

Foam of itself provides dilution by means of the water draining from the mass. This is a slow process and for deep spills may take too long to be practical. In several of the test programs already referenced it has been shown that water can be applied to the top of the foam to increase the drainage rate into the spilled material. This has to be in the form of a water fog to prevent excessive breakdown of the foam. Figure 9 shows this action for N_2O_4 and can be compared to Figure 8 above.



a. Free Spill

b. Foam Application



c. Foam Blanket in Place

FIGURE 6. VAPOR CONTROL SEQUENCE FOR N_2O_4 SPILL

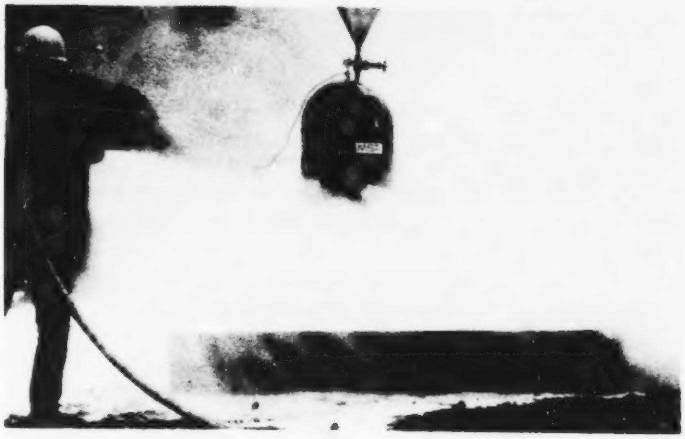


FIGURE 7. DIRECT WATER APPLICATION TO FOAM CONTROLLED SPILL OF $SiCl_4$

FIGURE 8. DIRECT WATER APPLICATION TO FOAM CONTROLLED SPILL OF N_2O_4

FIGURE 9. WATER FOG APPLICATION TO FOAM CONTROLLED SPILL OF N_2O_4

This technique is also a slow process but faster than foam alone. It has one complication. If a nonsoluble gas is being released, it will convert the draining water to a froth. This increases the foam volume slowly. If sufficient freeboard is not available within the containment, the foam can overflow. Termination of the water application will allow this action to subside, so that dilution can be restarted.

Water fog application through the foam blanket can be an effective means of dilution. Its use must be assessed in light of the spill scenario and the limitations of the technique.

One additional comment on foam and dilution should be made. For very reactive chemicals it may not be possible to develop a persistent foam cover. This is the case for sulfur trioxide.[4] Foam offers a mechanism to slowly add water to the spill with a minimum of reaction. For the period of time of foam application the downwind hazard may be exaggerated. In many cases the duration of the downwind hazard and the distance may be reduced. With SO_3, for example, the conversion is to an H_2SO_4 aerosol with a minimum of entrained vapor. The aerosol tends to settle out over shorter downwind distances than H_2SO_4 vapors created by SO_3 interaction with moisture in the air.

GENERAL COMMENTS

In concluding this discussion of the use of foam to control the vapor hazard of water reactive volatile chemicals, three general comments are in order.

The first relates to spill size versus foam quantity in test work. In several cases past work has shown results which are inconsistent with the preponderance of data. In most cases this is attributable to an inbalance of spill size and foam volume, with the latter being large in relation to the spill. For tests to be valid the spill volume should be large compared to the foam volume. If the water from the first foam application can dilute the spill to a nonhazardous condition, the test data do not reflect the true capabilities of the foam.

The second comment addresses the need for adequate foam capacity before considering foam as a mechanism for vapor control. In almost all cases with water reactive materials, the application of foam exaggerates the vapor release until such time as the foam blanket completely covers the spill. Thus the faster the rate of foam application the better. More important, however, is the availability of sufficient foam and foam capacity to achieve complete coverage.

The minimum effective foam application rate should be established for each foam-chemical combination. At present the limited data would indicate minimum application rates to be 1.3 m^3/minute of foam per square meter of spill surface for high expansion foam and 1.86 liters per minute of solution flow per square meter of spill for low expansion foam. Below these levels for medium or large spills foam degradation by interaction with the spilled chemical may be faster than the rate of advance of the foam blanket over the spill surface.

The last comment addresses the problem of foam degradation. Except in those cases where the foam gels, as in the hydrazine tests, foam degrades with time. There are two contributing actions--water loss through drainage and evaporation and reaction with the spilled chemical. In situations where the spill persists for a significant time, it will probably be necessary to reapply foam to maintain the blanket and the vapor control.

In some of the work referenced here, reapplication of the foam blanket has not always been successful. This has been attributed to a slowly increasing reaction violence as water drains into the spill. It is a function of the reactivity between the foam components, not necessarily the water alone. Where this situation exists, at some point in time the reactivity becomes so severe that further foam application is ineffective. It is important, therefore, in assessing the capabilities of any specific foam-chemical combination, to insure that the foam blanket can be maintained for prolonged periods of time. This is not established by single application foam tests. Several foams including commercial formulations were able to control N_2O_4 spills for 20 to 30 minutes but could not be effectively reapplied. The principal effort in the USAF program was to evolve a foam chemistry which allowed repeated makeups to provide several hours of control.

This makeup problem should be carefully addressed where mutual aid associations are involved. Changing foam chemistries during the spill period could result in loss of control if the new foam was incompatible with the chemical involved in the spill.

CONCLUSIONS

The capabilities of water based foams to control the vapor release from spills of volatile hydrocarbons is being extended to water reactive liquids including those with strong acidic or alkaline character. These developments involve special foam formulations. In most cases the so-called fire fighting foam materials are not applicable.

This technology will probably not be useful to responders to transportation incidents. It does hold promise as a spill control technique for in-plant or storage facilities where specific chemicals are involved. The first installations are now in service for $SiCl_4$ and the propellants hydrazine and nitrogen tetroxide.

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NEW TECHNIQUES IN CHEMICAL SPILL CONTROL

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Large quantities of hazardous materials are routinely handled by inland and marine transportation and support equipment. Spills during transit or at producer and user storage facilities pose serious threats to the health and welfare of the general public and the environment. Counteractive measures in such situations can be defined in terms of four elements: detection, surveillance, control, and recovery. The study summarized here investigates the possibilities for enhancement of these elements by use of fluorescent agents, sonic sensing (SONAR), and chemical agents capable of producing heats of hydration to promote thermal infrared (TIR) sensing. It is suggested that these techniques can be utilized synergistically with each other and with other conventional systems.

With regard to detection and surveillance of spills on water surfaces, excellent reviews on aerial (visual) observations and remote sensing systems in general have been published (see, for example, references (1-4). The following abstracted summaries of salient points in these reviews pertain to the present work.

> Direct visual observation of oil spills, while constituting the first line of any effort in spill control and recovery, suffers from the lack of real time data display; the virtual dependence on daylight; the likelihood of human error (e.g., in mistakenly identifying seaweed, blooms of planktonic organisms or other benign phenomenon as being oil or hazardous material spill; e.g., see reference (5)); and the limitations imposed by adverse weather. At the same time, it is most likely that actual control and recovery efforts will be most dependent on direct visual visual observation: the laying of booms and the operation of skimmer craft will long depend on eyesight observations, with remote sensing as a means of effecting detailed monitoring of such efforts not a very likely eventuality.
>
> Remote sensing is of increasing importance in initial detection of large spills in remote areas, and the surveillance of such areas to ascertain the effects of set, drift, dispersion, and similar factors in the movement and other natural disposition of such spills.

Thomson, Ross and Howard-Lock have stated: "the basic criteria for remote sensing surveillance are real time data display, all-weather capability and day or night operation. The ultimate system must be able to detect and identify the oil and/or species of oil. Some present sensors satisfy most of the basic criteria while others are more limited. Microwave and radar sensors are the only group that provide all weather operation, although real time data can be a problem and they do not positively identify oil. Visible range sensors are generally limited by weather and to daytime operation. Active light sensors (i.e., lasers) help to overcome these deficiencies. At the present time the fluorescent and Raman spectral properties of oil provide the best avenues of research toward definitive identification of the oil. Any surveillance system must, therefore, consist of all or some reasonable combination of the sensors in order to maximize its operational capability."(2) (See Table 1.)

TABLE 1. SENSOR CAPABILITIES AND SURVEILLANCE REQUIREMENTS (Ref. 2)

			REAL TIME VIEWING	DAY / NIGHT	ALL WEATHER	APPROX. SPATIAL RESOLUTION (mrad)	EASE OF RECTIFICATION	LARGE AREA COVERAGE	DETECTION		AREA MAPPING		COVERAGE	IDENTIFICATION OIL TYPE	THICKNESS	RATE OF MOVEMENT
ULTRAVIOLET		CAMERA	X	D	HFCR	0.01 to 0.1	1	X	G		G		F	X	•	S
		SCANNER	✓	D	HFCR		3	X	FG		FG		P	X	•	
		VIDEO	✓	D	HFCR		2	X	G		G		P	X	•	
VISIBLE	CAMERA OR SCANNER	0.40 - 0.50 μm	X	D	HFCR	0.001 to 0.01	1/3	X	FG		FG		F	X	X	S
		0.50 - 0.58	X	D	FCR		1/3	X	F		F		P	X	X	
		0.58 - 0.62	X	D	FCR		1/3	X	P		P		P	X	X	
		0.62 - 0.70	X	D	FCR		1/3	X	P		P		P	X	X	
	CAMERA	COLOR	X	D	HFCR		1	X	F		F		P	X	X	
		COLOR INFRARED	X	D	FCR		1	X	FG		FG		P	X	X	
		POLARIZED	X	D	HFCR		1	X	G		G		P	X	X	
		VIDEO COLOR	✓	D	HFCR	>0.01	2	X	FG		FG		P	X	X	
INFRARED		3.5 - 5.5 μm	✓	DN	FCR	1.0	3	X	FG		FG		P	X	•	S
		8 - 14 μm	✓	DN	FCR		3	X	G		G		P	X	•	
PASSIVE MICROWAVE		RADIOMETER	✓	DN	R	-	-	X	G		F		P	X	•	S
		SCANNER	✓	DN	R	10.0	4	X	G		F		P	X	•	
RADAR		X BAND	•	DN	A	10.0	3	✓	P	F	P	G	P	X	•	S
		C "	•	DN	A		3	✓	P	P	P	P	P	X	•	
		P "	•	DN	A		3	✓	P	F	P	G	P	X	•	
		L "	•	DN	A		3	✓	P	F	P	G	P	X	•	
									H	V	H	V				

X - NO ✓ - YES
A - ALL WEATHER
D - DAY ONLY
DN - DAY & NIGHT
F - FAIR

• - POTENTIAL FOR DEVELOPM'T
G - GOOD
P - POOR
H - HORIZONTAL POLARIZATION
V - VERTICAL POLARIZATION

FCR - LIMITED BY FOG, RAIN & CLOUD
HFCR - " " " " CLOUD & HAIL
R - " " RAIN
1-4 - RELATIVE EASE OF RECTIFICATION
S - PROVIDED BY SEQUENTIAL COVERAGE

O'Neill, Neville and Thomson provide excellent descriptions of state-of-the-art sensor systems, particularly in terms of the types of equipment which should be considered for inclusion in the sensor package, i.e., side-looking radar; low light level television and dual channel scanner with UV and IR detectors; laser fluorosensor; and suitable photography. (3,4)

With regard to (UV) fluorescence systems, two general applications would seem to pertain: remote sensing surveillance, and use of fluorescent agents to enhance visibility in night-time spill control and recovery operations. Considerable research and development have been extended to the former (cf., e.g., references 3, 4, 6 and 7 and references cited therein); less attention has been devoted to the latter (cf. references 8,9).

Heretofore, it would appear that these UV fluorescent techniques would be applicable almost exclusively to oil spills, and then with varying degrees of efficiency. Thus, O'Neill, Neville and Thomson have stated (remarks abstracted): Few molecules exhibit fluorescence; of those that do, the aromatic hydrocarbons are important, this class of compounds exhibiting fluorescence in oils. Typical oil fluorescence spectra are shown in Figure 1. Oils can be distinguished from other fluorescent materials (e.g., photoplankton) by spectral comparisons. Additionally, oils of different types (light, heavy, etc.) can be differentiated.

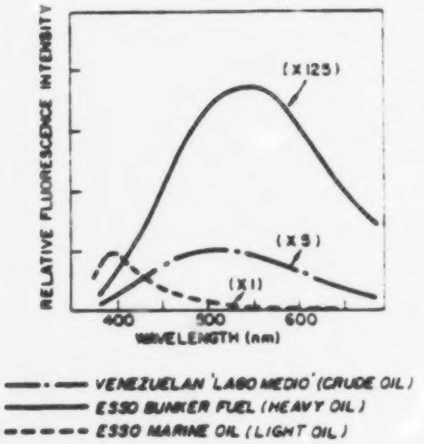


Figure 1. Typical Oil Fluorescence Spectra
(cf. Reference 3)

In 1978 Fingas initiated research and development of a practical means of providing sufficient illumination of oil spills on water surfaces utilizing commercially available UV sources to produce sufficient visible fluorescent illumination from the oil to permit discernment of oil patch perimeters on the water surface. His work resulted in development of a cheap, portable unit which would be effective at distances up to 144 meters, and demonstrated that somewhat more powerful units could easily be fabricated with operational efficiencies at up to twice this distance. (8)

For oil spills, the UV fluorescence system is obviously highly practical for both surveillance and operational illuminative applications. As is indicated in Table 2, however, the majority of those liquid organic determined

TABLE 2

LIST OF PRIORITY HAZARDOUS MATERIALS FOR THE ENVIRONMENTAL EMERGENCY BRANCH

(cf. reference 10)

*		Aminocarb Pesticies
*	**	Benzene
*		Butyl Aldehydes
		Creosote
		Cumene
*		Cyclohexane
*		Dimethyl Terephthalate
*		Estemine
	**	Ethyl Benzene
*		Ethyl Chloride
*		Hexane
*		Latex
*		Methyl Isobutyl Carbinol
*		Methyl Isobutyl Ketone
*		Methyl Methacrylate
	**	Styrene
		Tall Oil
		Terphenyls
	**	Toluene
*		Triallate Pesticides
*		Trifluralin Pesticides
		Turpintine
	**	Xylenes
*		2-Ethylhexanol

*Insufficient fluorescence for practical remote sensing applications.

**These items were included in the highest priority hazardous materials list; all other items were included in the second grouping of priority chemicals.

NOTE: The original lists were culled to exclude inorganic chemicals, and materials with melting points above 40°C; specific gravities above 1.1; boiling points below 0°C; and water solubilities of more than 10%.

to be priority hazardous materials by the EPS are not sufficiently (if at all) fluorescent for either surveillance or operational illuminative work. For many materials (both petroleum and hazardous materials in general) which are fluorescent, the emissivities are frequently low by comparison with more efficient fluorescers. Thus, it would be highly desirable to be able to "dope" spills in general with an efficient fluorescer to enhance the fluorescent signal on the one hand (for remote sensing), and to increase the amount of fluorescent illumination for night-time spill control and recovery operations on the other. Use of such an agent or agents would be desirable from other standpoints as well. Thus, the fluorescent emission wavelength would always be a known factor, onto which a remote sensing unit could be locked. Use of different agents with different fluorescent wavelengths would permit time studies involving effects of set and draft within a large spill mass, determination of appearance of "new" spill material within a general spill area, and disappearance patterns arising from recovery efforts and dispersion of oil into the water column. Optimum fluorescent agents should be cheap, non-toxic, efficient, easily soluble in oil, and stable. For operational illumination in spill recovery and control efforts the fluorescent emission should be as close as possible to 550 nm, at which wavelength the human eye has maximum perception of visible light; see Figure (2).

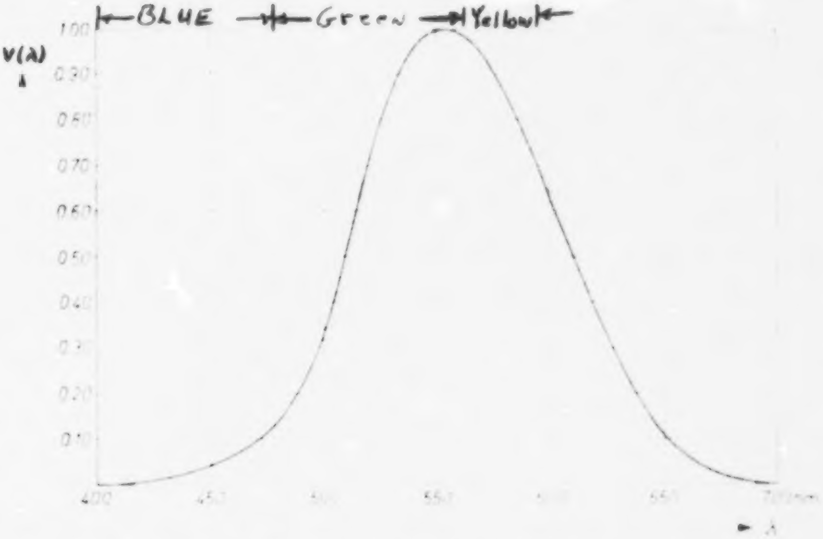


Fig. 2. Eye sensitivity V(λ) as a function of the wavelength λ. The maximum is arbitrarily given the value 1.00 (Ref. 11)

A possible disadvantage in the use of fluorescent doping agents is the occasional quenching effects which can be exerted by some substrates on the fluorescent activity of a given agent. Usually such quenching effects are not universally exerted on all fluorescers, however; and the availability of several efficient fluorescent candidates for given situations should obviate the occasional problems which might thus arise. By far the most difficult problem confronting any possible use of such agents has been the dilemma posed by the oleophilic requirement for such agents: the fluorescer when applied over a water area with intermittent oil patch coverage should dissolve easily in the oil, and at the same time not float undissolved on the water surface (thereby preventing discernment of the oil patch perimeters). Moreover, the requirement for high efficiency for the fluorescer is predicated on the desirability for application of very small concentrations of the fluorescer in the oil or hazardous material; it is usually quite difficult to apply very small quantities of agents uniformly over very large areas.

Our group initially attacked this problem by investigating the use of solvents which would be miscible in both oil and water and also would dissolve appreciable quantities of the fluorescer. It was found, for example, that the widely used stilbene optical brightener UVITEX OB^{TM} (CIBA-GEIGY Corporation), and the proprietary 131SC$^{(TM)}$ (MORTON Chemical Company), could be dissolved in glycol ether solvents and then sprayed over oil/water surfaces. Where the spray solution encounters oil patches, the fluorescer dissolves readily into the oil (or hazardous material); where the spray solution encounters open water, the solution quickly dissipates into the water column with no surface residue. The glycol ether solvents pose some toxicity problems, and considerable fire hazards in spraying; hence, this form of delivery was abandoned. Our group's more recent work has been directed to incorporation of the agents into dust formulations, the best of these being 48-mesh gypsum ("Plaster of Paris"; calcium sulfate) with 3% fluorescer intimately combined by mechanical dry mixing. Dusting of this formulation over spill areas gives even better results than the liquid spraying systems: on spill patches, the dust particles remain at the surface long enough for the fluorescer to dissolve off into the organic liquid contaminant, before the gypsum particles finally sink into the water column. In open water the fluorescer/gypsum particles sink almost immediately into the water, with no surface residue. Upon illumination with low-intensity long wavelength (336 nm) UV light the resulting low concentrations of fluorescer in the hazardous material spill provide sufficient visible illumination to provide vivid, easily discernible and very precisely delineated gleaming patch areas; see Figure 3.

UVITEX OB has the distinct advantages as being of demonstrated low toxicity and commercially available, in wide use. Although its emission wavelength (435 nm; see Figure 4) corresponds to low visual perceptivity (see Figure 2), this agent has been demonstrated to give overall excellent performance in two sea trials (to be discussed later in this report). 131SC is also an item of commerce in wide usage, of probably low (but not well documented) toxicity. It is much more easily soluble in organic solvents than UVITEX OB, and provides excellent visual perceptibility in its fluorescent emission, and the capability of being excited at easily attainable low wavelength visible light (see Figure 5).

As can be seen in Figure 4, UVITEX OB has enough of its excitation band in the 337 ± 10 nm band to accomodate the nitrogen laser assembly currently in use in remote sensing systems; there is a loss of only about 55% of the emissivity in lowering the excitation wavelength from this agents maximum excitation wavelength of 375 nm to the 337 nm characteristic of nitrogen lasers. Thus, UVITEX OB could be a strong candidate for use in enhancing signals in remote sensing activities.

The use of powdered gypsum as a carrier for the fluorescer enables the facile homogeneous distribution of the fluorescer, itself in small quantities incorporated in the larger mass of gypsum, over very large spill areas by means of conventional crop dusting techniques. The gypsum base is entirely non-toxic and with no fire or other similar hazardous effects.

Lighting assemblies of various types have been tested and proven effective for these fluorescent agents. For UVITEX OB, which requires 366 nm excitation sources, a close-packed array of seven 100-Watt PAR 38 Sylvania mercury vapor spotlights, each focused on a common target at infinite distance, and each equipped with a purple filter manufactured by Ultraviolet Products, Inc. Each unit is also ballasted with an individual 10 mfd 100-Watt 120-Volt Advance$^{(R)}$ transformer unit. (See Figure 6.) Although this lighting unit could be used at any elevation, it would be deemed most practical for most spill control and recovery operations to have as vertical an attitude toward the spill area as possible; one possible means of lighting, from an overhead helicopter, is illustrated in Figure 7. This unit has been tested at

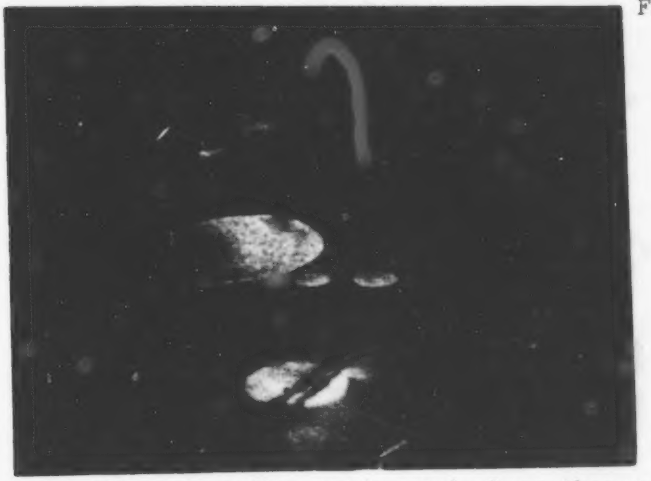


Figure 3. A 5' x 12' pool filled with water, and with 550 ml of light mineral oil applied in patches covering about 10% of the pool. 16.0 g of 3% Morton 131SC fluorescer mixed with 97% 48-mesh gypsum was dusted over the entire area. Where there were no oil patches the fluorescer quickly fell to the bottom of the pool; where there was oil a concentration of 80 ppm of fluorescer in the oil was readily achieved in less than one minute by dissolution of the fluorescer into the oil. On illumination with two 400-Watt Sylvania mercury vapor lamps with not phosphor coating, fluorescent illumination from the patches at 539 nm (yellow-green) was readily discernible, with excellent capabilities for discerning the patches.

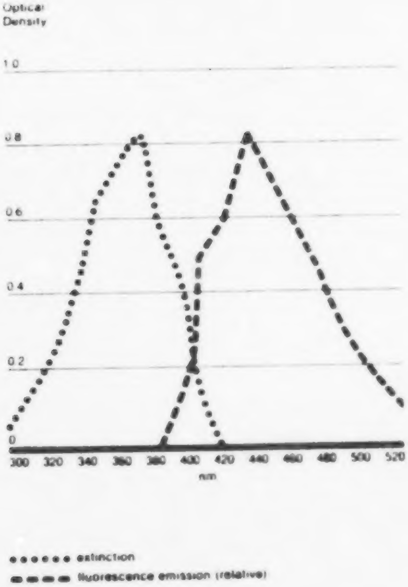


Figure 4. Fluorescent excitation/emission spectrum for CIBA-GEIGY UVITEX-OB.

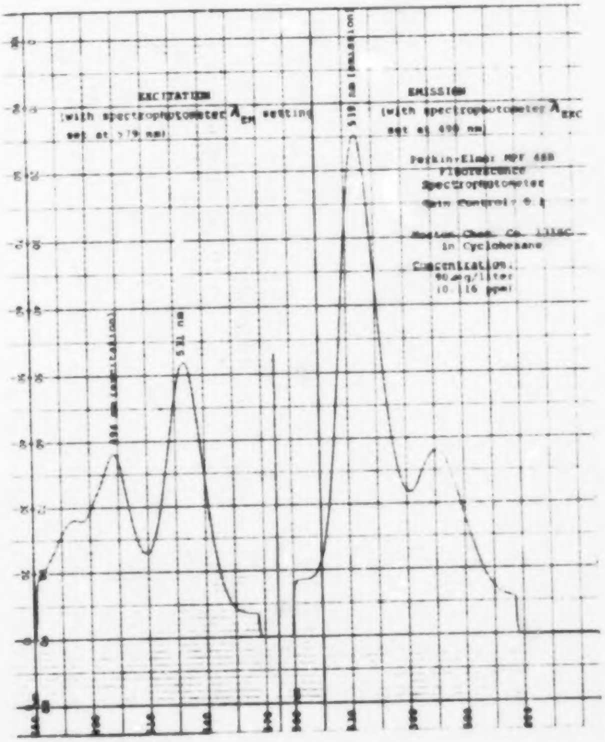


Figure 5. Fluorescent excitation/emission spectrum for MORTON 131SC.

land and also at sea (see below) with excellent results at rather large distances, effectiveness being demonstrated up to 100 meters for an assembly with only six lamps. Moreover, in the sea trial to be discussed, the lamp assembly was mounted at a very low elevation with an angle of incidence of the lamp beam to the spill area of only about 5°; at this very shallow angle it is likely that fluorescent patches on the tops of waves were the more prominent sightings. The geometry of the light beam from the seven-lamp rack is also indicated in Figure 7. The low intensity of the UV light at operational distances is well within accepted exposure levels (cf. Fingus in reference 8), although personnel located within a few feet of the lamp would require eye and skin protection in the form of goggles, clothing and skin creams.

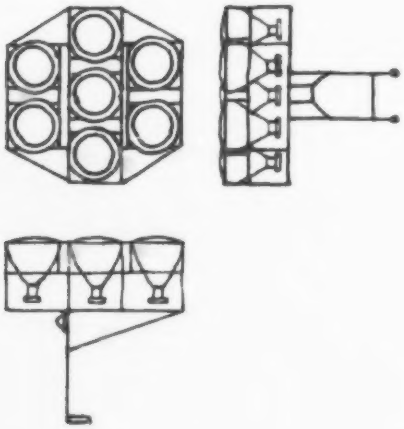


Figure 6. Orthographic projection of assembly of seven 100-Watt PAR-38 UV lamps.

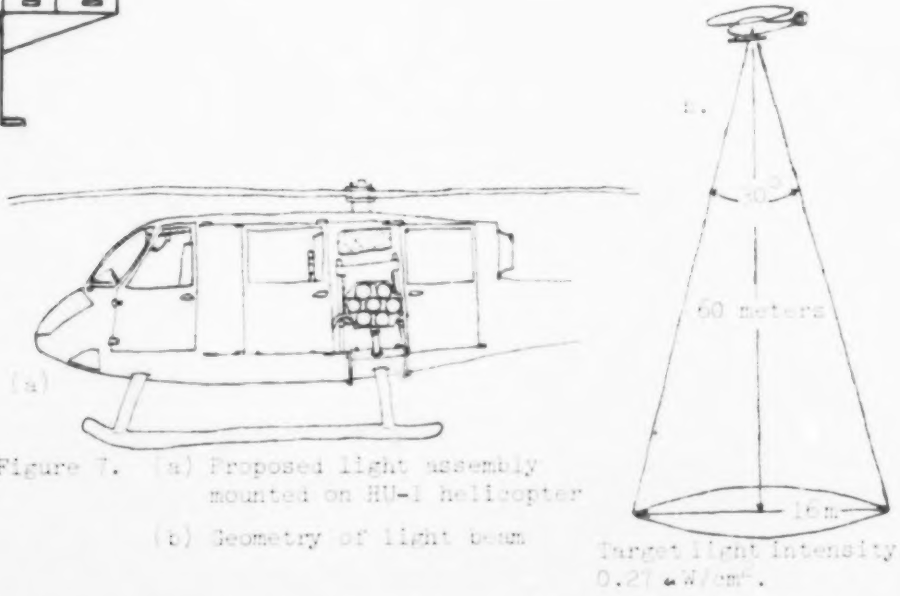


Figure 7. (a) Proposed light assembly mounted on HU-1 helicopter

(b) Geometry of light beam

Sonic sensing (SONAR) techniques have not been as extensively investigated or utilized as have the systems previously mentioned. Proni has stated: "The use of acoustics in studying oceanic pollution problems has risen substantially in the last five years. Since that time numerous uses of acoustics have been made in studying dumped materials (including) sewage sludge, dredge material, petrochemical wastes, industrial wastes, pharmaceutical wastes, sub-surface oil (from the IXTOC-1 oil spill), and, recently, drilling muds." (12)

Additional remarks by M.H. Orr are abstracted as follows: "Remote acoustic sensing of atmospheric process has developed into an active research discipline. In contrast, the number of researchers using high frequency remote acoustic sensing to study oceanic fluid processes is quite limited. This may be due to the past preoccupation of trying to understand oceanic circulation on a mesoscale and also in interpreting acoustic records without complementary *in situ* data. It would appear (however) that the use of a device which can be carried at the surface of a water column to give information in real time about particle densities at every depth would have appeared. Such a device, high frequency acoustic echo sounding and sensing equipment does exist and its practicability has been demonstrated. These techniques have the potential for becoming a valuable tool in oceanographic research and monitoring exercises, working in both a complementary and a stand-alone format." (13)

In addition to work performed on the IXTOC-1 spill, some work has been performed on detection of oil under ice (14,15). Our group was successful in demonstrating the synergistic effects to be derived in utilization of sonic sensing techniques in conjunction with fluorescent illumination for detection and surveillance work, as described in reference (9) and summarized in remarks to follow in this report. During the Newfoundland Oil Spill Dispersant Sea Trial of October 1981, performed by Intera Environmental Consultants, Ltd. under the auspices of the Environmental Protection Service and Canada Centre for Remote Sensing, it was observed in one of the trials that the dispersant (Corexit 9527) had only momentary success in dispersing the spill material into the water column. Shortly after being sprayed onto the spill area, the spill quickly submerged into the water column, to an unknown depth, and then very quickly re-emerged (maintaining almost all details of its original contours). It was speculated that the spill material tended to shed the dispersant once submerged in the water column, although this was not a firmly established rationale. (16) The use of sonic sensing would be particularly useful in following the fate of spill material undergoing either natural or artificially induced dispersion. Moreover, in any spill situation, a large proportion of material will be found near, rather than at the water surface. This is particularly true of high density, low viscosity, and/or high polarity (and thus more soluble) hazardous materials, and of course will be particularly the case also in more turbulent wave than under calm conditions. The rate of dissipation of hazardous materials into the water column is of great importance from ecological as well as from recovery standpoints. Thus, underwater sonic sensing techniques were shown to be very useful in locating near-surface spill material in the IXTOX-1 spill.

The high frequency underwater acoustic echo sounding and sensing equipment utilized by our group is described below, and illustrated in Figure 8. Figure 9 depicts a typical two-channel recording of sonic sensing data acquired in detection and surveillance of hydrocarbon plumes in an estuarial exercise.

Component Description Model DFT-210 Transceiver

The high power, two channel calibrated transceiver generates two independent transmit signals over a frequency range between 3kHz and 300 kHz. Dual channel low noise, high gain receivers provide calibrated outputs which incorporate accurately controlled time varying gain to compensate for

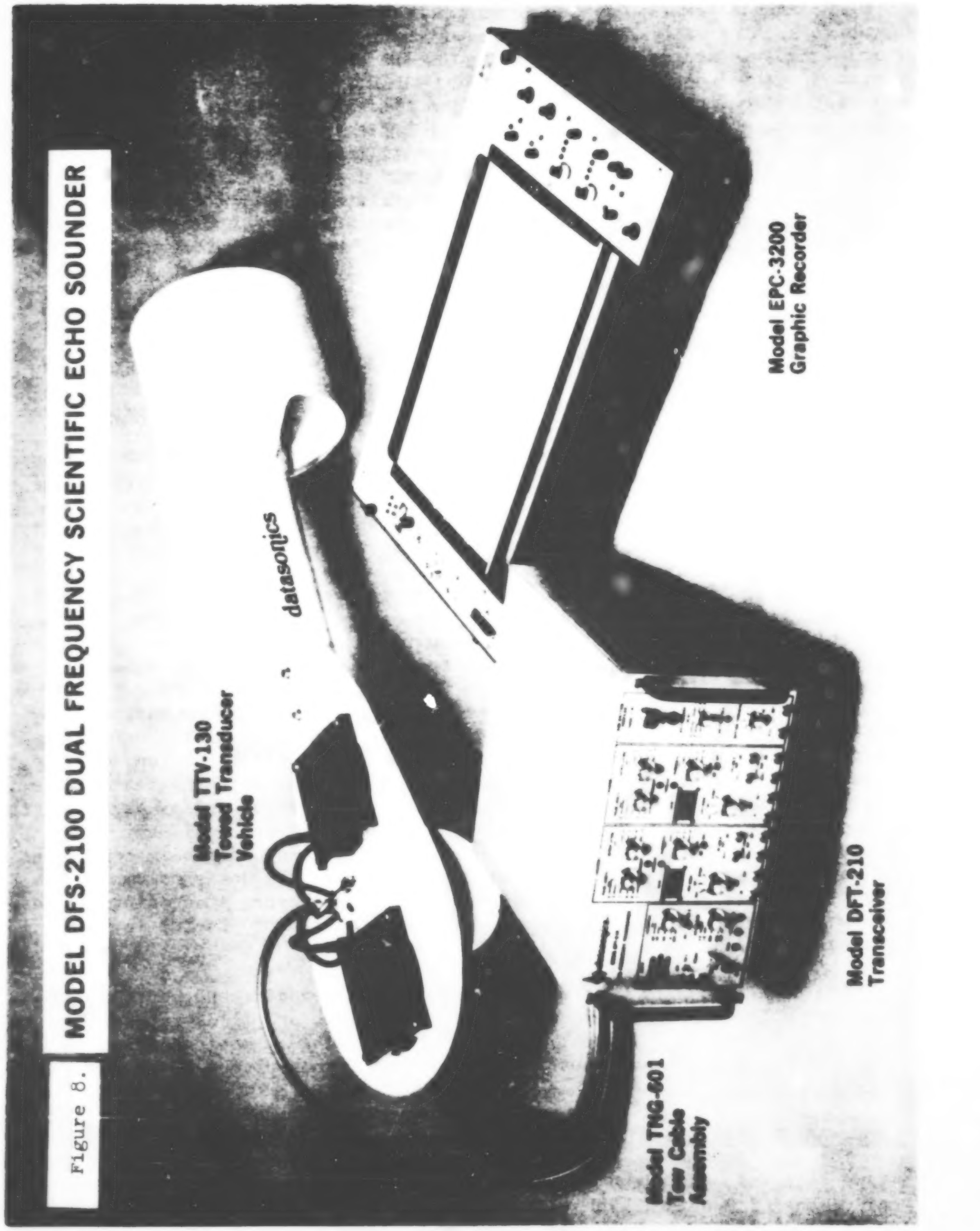
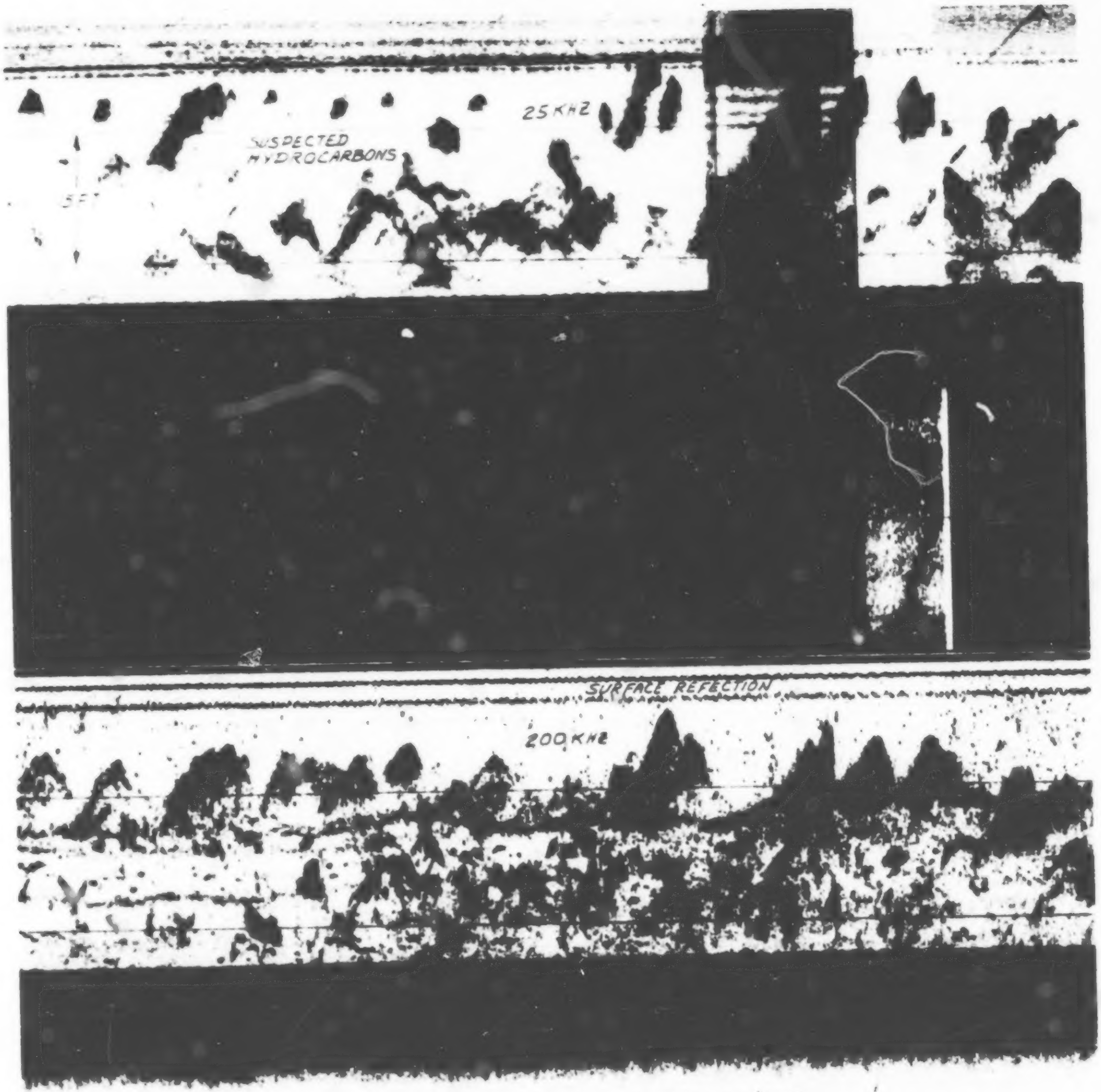


Figure 8. MODEL DFS-2100 DUAL FREQUENCY SCIENTIFIC ECHO SOUNDER

Model TTV-130
Towed Transducer
Vehicle
datasonics
Model EPC-3200
Graphic Recorder
Model DFT-210
Transceiver
Model TNG-601
Tow Cable
Assembly



DATASONICS MODEL EES-20/200
ENVIRONMENTAL ECHO SOUNDER
LOCATION: CHESAPEAKE BAY/ANNAPOLIS
VESSEL SAILING VESSEL R/V WOLVERINE
SPEED: 5KN
SCALE: 15 FT/DIV
RECORDER: EPC MODEL 3200
RECORD COURTESY FRYLING TECHNICAL SERVICES

Figure 9. Mapping the structure of an estuary or coastal water body. The record shows distinct salinity stratification in the lower 200 kHz portion while the upper 25kHz record emphasizes plumes of suspected hydrocarbon or sewage plumes which could be caused by numerous anchored coal colliers waiting to proceed into Baltimore Harbor.

spreading and attenuation losses. Wide system dynamic range allows processing of large and small scatterers throughout the water column.

Model TTV-130 Towed Transducer Vehicle

A lightweight two fish with two transducers installed for operation at customer specified frequencies between 3 kHz and 300 kHz. Constructed from corrosion resistant stainless steel and fiberglass, the vehicle can be easily deployed and recovered by a single person.

Model EPC-3200 Graphic Recorder

A 19 inch dry paper two channel recorder for simultaneous display of data at the two selected system operating frequencies. The recorder has an internal data memory which allows selective data expansion and display of water column or sub-bottom sediment data in the best possible format. Memory capability allows data display free of interference problems associated with second bottom multiple echos.

Tow Cable Assembly

Tow cables are available in different lengths with either external armoring or a Kevlar braid with urethane jacket to provide the required breaking strength. A stainless kellums grip or molded epoxy retention provides a termination at the tow fish end of the cable. High quality Brantner Sea-Con connectors are utilized. Internal dedicated coaxial conductors provide best isolation between channels with lowest possible noise insetion.

THERMAL INFRARED RADIATION (TIR)

With regard to thermal infrared radiation, the following remarks provided by T. Alföldi of Intera Environmental Consultants, Ltd. pertain:

> The measurement of emitted radiance in the thermal infrared (TIR) portion of the electromagnetic spectrum (4 to 20 µm) is a particularly useful mechanism for identifying oil targets in a marine environment. Besides providing an independent dimension of oil/water discrimination it is one of the few spectral bands in which passive sensors can be used in darkness. The complex mechanisms affecting the relative radiances of oil and water in the TIR band are well described by O'Neil et al. (3) The physical temperature and the emittance of the targets will define their relative radiation emission magnitudes. The emittance factor is influenced by such variables as thin film interference (constructive and destructive), surface reflectance, and bulk oil emissivity. These variables change in their impact on oil emittance, depending on the thickness of the oil layer. (17)

For thin (e.g., sheen) films of organic fluids on water surfaces, the thermal emissivities are routinely less than that of water alone; hence, very thin films should normally appear to be cooler in radiant temperature than the surrounding water. Thicker films of organic liquids will be affected by greater retention of heat attained by solar radiation than the surrounding water, due to lower heat capacities and thermal conductivities, and by the reduced rate of evaporation of water under the oil cover. Thus, thicker films will "appear" warmer than surrounding water, and the thicker portions of the patches may be viewed as a warm area surrounded by a cold halo of sheen, itself surrounded by water of intermediate apparent temperature. (See Figure 10.)

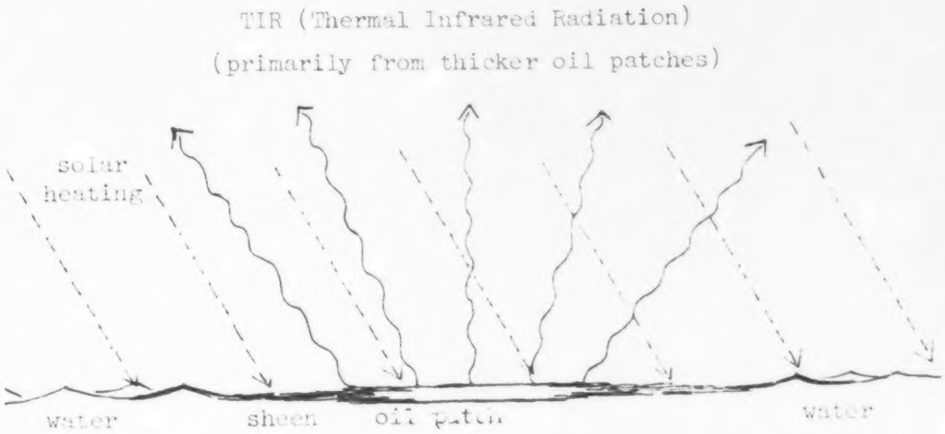

TIR (Thermal Infrared Radiation)
(primarily from thicker oil patches)
solar heating
water
sheen
oil patch
water

Figure 10. Slow interfacial heat transfer from thicker spill patches into underlying water column, decreased water evaporation in patch areas, and solar heating of the patches tend to increase apparent patch temperatures.

There are potential problems in application of TIR in a variety of spill situations. Thus, upwelling of cold water beneath spill patches (or into warm water in open water areas) could serve to decrease capabilities for discrimination of patches. Likewise, passage of cold (or hot) air masses could have similar overall effects (although it has been demonstrated also that spill areas tend to hold their heat differentials for hours, in many cases). Moreover, the lack of solar heating in high lattitude areas during late Fall, Winter or early Spring would appreciably diminish the potential for application of this technique during these seasons.

As it was proven feasible and potentially advantageous for the external application of fluorescent agents to enhance fluorescent sensing techniques, our group also considered that it might be possible to enhance the TIR from chemical spills by means of externally applied (e.g., by crop dusting) of agents which would provide appreciable heats of hydration on contact with water immediately underlying the spill patch. Properties which were deemed necessary for potential candidates for such applications include: high heat of hydration per gram of material; non-toxicity; non-corrosiveness; non-flammability; and low cost commercial availability. On the basis of our subsequent investigations, to this list should be added high solubility in water for the agent, and rapidity of hydration.

Tests were conducted at the U.S. Army Materials and Mechanics Research Center, Watertown, Massachusetts, using an Inframetrics 525 thermal imaging system directed at a 32 cm x 38 cm shallow metal pan containing water to a depth of about 2.5 cm, onto the surface of which had been applied 12 ml of heavy mineral oil in several floating patches. Thermocouple leads were situated at strategic locations at the water surface, at the surface in the middle of an oil patch, and in the middle of the water column, with temperature readings being recorded on a multi-channel recorder. When the oil/water surface readings had equilibrated to 23.3° C ± 0.2° (the oil being slightly warmer), 2.4 g of finely divided sodium oxide was dusted over the entire surface, with thermographic TIR results recorded on video tape along with the thermocouple recordings. Excellent thermographic correlations resulted; the thermocouple readouts are provided in Figure 11, below.

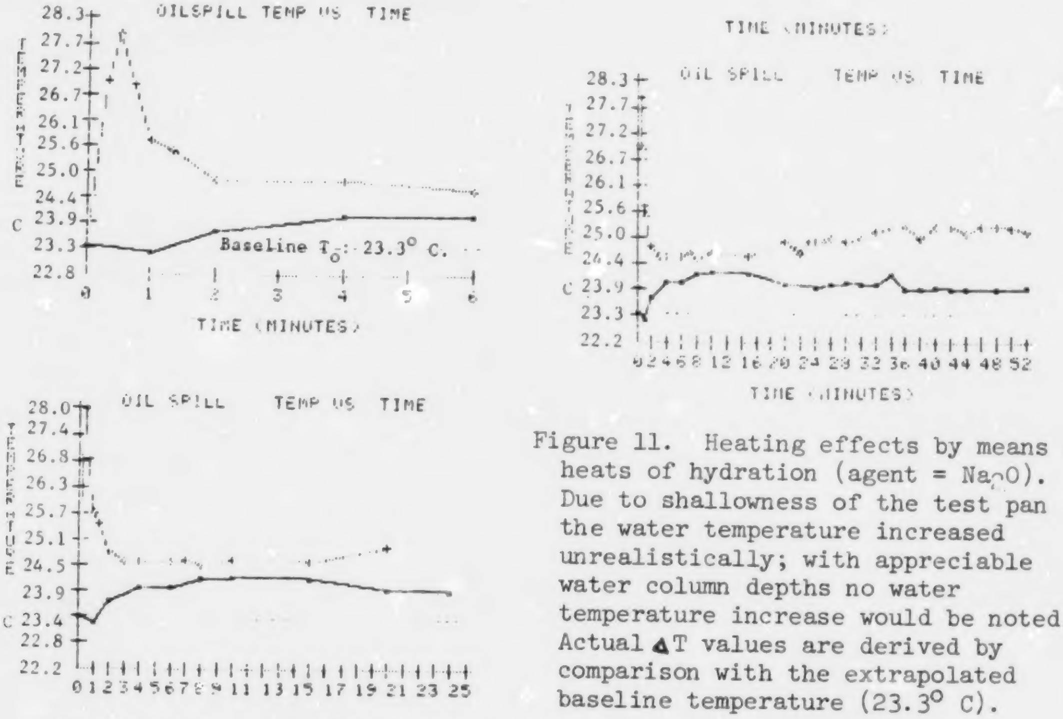


Figure 11. Heating effects by means of heats of hydration (agent = Na_2O). Due to shallowness of the test pan the water temperature increased unrealistically; with appreciable water column depths no water temperature increase would be noted. Actual ΔT values are derived by comparison with the extrapolated baseline temperature (23.3° C).

In estimating the efficiency of conversion of heat of hydration to TIR, the following assumptions are made:

spill material parameters
density = 0.8 g/cm^3
spec. ht. = 0.5 cal/g·°C
spill thickness = 0.2 cm

$\Delta T_{obs} = 1.7\ ^{\circ}C$ (see Fig.11)

Na_2O
$\Delta H = -887$ cal/g
(reference 18)

Total heat available = (wt.)($\Delta H_{hydration}$)
= (2.4 g)(-887 cal/g)
= 2129 cal.

$$\text{Efficiency} = \frac{(\text{Pan area})(\text{film thickness})(\text{Spec.Ht.})(\Delta T_{obs})}{\text{Total heat available}} = \text{ca. } 8\%$$

Sodium oxide is too exothermic a reagent for consideration for use in cropdusting situations at sea. Other cheaper, less exothermic (and some

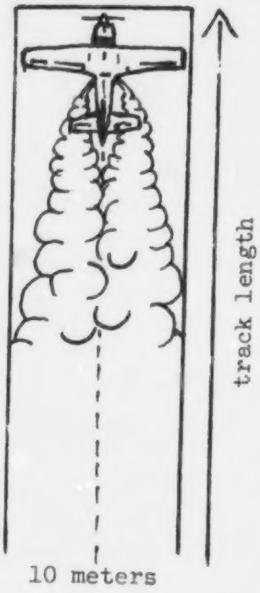


TABLE 3. HEATS OF HYDRATION TO ENHANCE TIR

	Agent	$\Delta H_{hydration}$ cal/g; ref. 18	Coverage by 500 kg agent on 2 mm spill; $\Delta T = 0.5^\circ$ C; TIR efficiency = 4%	
			Area (hectares)	Length of 10 meter track (kilometers)
exothermic agents	Na_2O	- 887	4.4	4.4
	$MgCl_2$	- 378	1.9	1.9
	CaO	- 325	*	*
	$FeCl_3$	- 257	1.2	1.2
	$CaCl_2$	- 153	0.7	0.7
endothermic agents**	NH_4HCO_3	+ 80	0.4	0.4
	NH_4NO_3	+ 78	0.4	0.4

endothermic) reagents are currently being investigated as candidates for application in enhancement of TIR sensing. Table 3 is a compilation of some of the more interesting of these; some (e.g. $MgCl_2$) appear to show great promise. Others, such as CaO (asterisked * above), and the endothermic ammonium bicarbonate and nitrate (double asterisked ** above) would appear to sufficiently energetic in terms of heats of hydration. Calcium oxide proved too insoluble and far too slow in rate of hydration to provide any discernible TIR effect, however; and the endothermic reagents, while momentarily effective, could not produce a lasting cooling effect on the thicker oil films. Apparently, in the latter case, the reduction in rate of evaporation of the underlying water as a result of the spill cover counteracted the cooling effect of the endothermic reagents. (In Table 3 the areas of coverage were derived by means of the same expression as was used in estimation of TIR efficiency, preceding page; TIR efficiency was assumed to be 4%, vice the 8% found in the laboratory experiment; a temperature increase of 0.5° C was assumed, since elevations of 0.4° C are near the lower limit of discrimination by existing equipment. Light crop dusting planes routinely carry hopper loads in excess of 500 kg of dry agent; heavier aircraft, such as the Thrush Commander, can carry payloads of 1000 kg. Track widths of 10 meters are fairly routine for low-flying crop dusters.)

SEA TRIALS ABOARD EPA OSV ANTELOPE (SEPTEMBER 1981 AND JUNE 1983)

In September 1981 enough promising results had been realized to warrant an initial test at sea, in an extrapolation from the laboratory work by our group on fluorescent and sonic sensing techniques. In this first test aerial dusting techniques were not utlized; the fluorescent agent was added directly to the fish oil used for the spill. A second test was conducted in June 1983 to demonstrate the feasibility of distributing the fluorescer as a dust cloud, onto the spill area. Both tests were conducted in Cape Cod Bay; summaries of test results are presented in Tables 4 and 5.

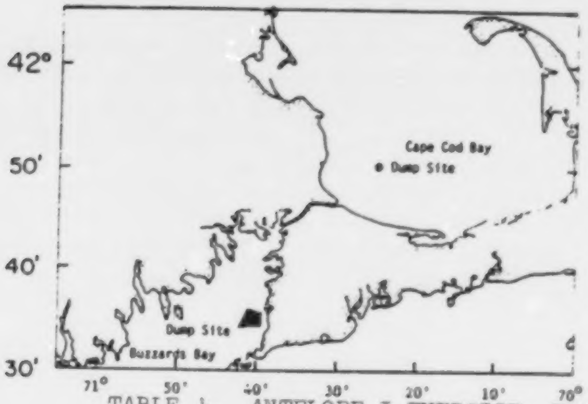


Figure 12. Cape Cod Bay Dump Site, location of both 1981 and 1983 ANTELOPE sea trials. In both tests the EPA OSV ANTELOPE, a 50-meter ocean survey and research ship, was used as the main research vessel. In the 1983 test an auxiliary craft, an 18 meter buoy tender (MARITIME QUEST) operated by Massachusetts Maritime Academy, was also used as the target vessel.

TABLE 4. ANTELOPE I EXERCISE, FLUORESCENT AGENTS/SONIC SENSING
CAPE COD BAY, MASSACHUSETTS 14 SEPTEMBER 1981

Time: 9:30 - 10:15 PM

Ship Speed: 4 kts (7.3 km/hr)

Weather: Temperature: 15° C

Wind: 5 kts (9.1 km/hr)

Waves: Calm

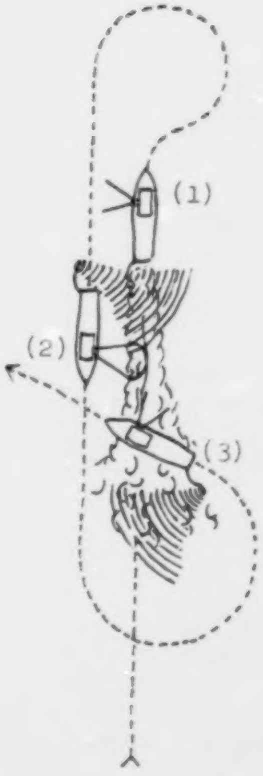
Visibility: Full moon, occasional squalls with cloud cover

Spill: 113 liters fish (menhaden) oil; SG = 0.93

Fluorescer: UVITEX OB™ (CIBA-GEIGY); 0.8 g dissolved in fish oil to provide 76 ppm concentration

UV Lamps: One 565-Watt Hanovia sun lamp (2% of power in 366 ± 5 nm band

SONAR: DATASONICS DFS-210 Dual Frequency acoustic sensing system



SUMMARY OF EXERCISE:

(1) ANTELOPE lays doped oil on water from stern; proceeds 1000 meters, performs Williamson turn to port.

(2) ANTELOPE passes spill 30 meters to port. Spill easily observed from 50 meters ahead to 50 meters astern. Independent simultaneous pick-up of sonic sensing signals; SONAR operators were isolated from knowledge of visual sighting of fluorescent slick.

(3) ANTELOPE crosses spill track 15 minutes later; very poor visibility of fluorescent slick. SONAR operators report enhanced signal; apparent dispersion of heavy fish oil into water column.

TABLE 5. ANTELOPE II EXERCISE, FLUORESCENT AGENTS (AERIAL DELIVERY)
CAPE COD BAY, MASSACHUSETTS 13 JUNE 1983

Time: 10:30 - 11:30 PM

Ship Speed: 4 kts (7.3 km/hr)

Weather: Temperature: 15° C

Wind: 25 kts, gusting to 35 kts (46 - 64 km/hr)

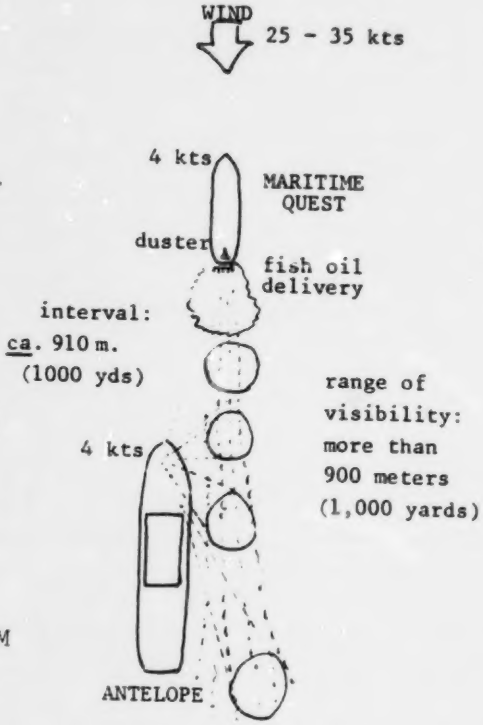
Waves: 0.6 meter bay chop

Visibility: No moon; squalls; clouds.

Spill: 170 liters fish (menhaden) oil; S.G. = 0.93

Fluorescer: UVITEX OB™ (CIBA-GEIGY); 45 g mixed with 1.5 kg 48 mesh gypsum (97% gypsum, 3% UVITEX OB)

Dusting Equipment: SEARS Heavy Duty SHOP-VAC™ industrial vacuum cleaner, operated in reverse.


WIND
25 - 35 kts
4 kts
MARITIME QUEST
duster
fish oil delivery
interval:
ca. 910 m.
(1000 yds)
range of visibility: more than 900 meters (1,000 yards)
4 kts
ANTELOPE

UV Lamps: Six 100-Watt PAR 38 Sylvania mercury vapor spot lights in rack mounted on video camera tripod for ease in tracking. About 5% of wattage is in 365 ± 5 nm band.

Summary of Exercise:

(1) Buoy tender (MARITIME QUEST) lays oil from stern; fluorescent dust is blown from 02 level of buoy tender over general spill area, as fish oil is laid; most of dust was blown off track by high winds.

(2) Vivid fluorescence easily discerned from spill area, from ANTELOPE, 100 meters ahead and astern, 50 meters to starboard. (See Figure 13.)

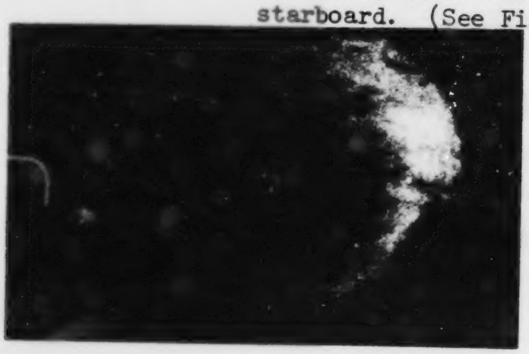


Figure 13. View of fluorescent spill (approximately 25 meters distance).

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REVERSE OSMOSIS IN CHEMICAL SPILL CLEAN-UP

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INTRODUCTION

Most transportation rights-of-way in Canada contain or are contiguous to small bodies of water. A soluble chemical spill into these waters can therefore produce large quantities of dilute chemical solution. Current methods of cleanup require removal and disposal, preceded where necessary by neutralization. Any method which will reduce the volumes of aqueous solution to be handled will result in improvement. Reverse Osmosis promises to be a method of substantially reducing the volumes to be transported for tratment/disposal.

Reverse Osmosis involves the concentration of chemicals by their physical removal from the solvent, usually water. It has, to date, been used primarily for the desalination of salt and brackish waters for drinking but the number of industrial uses is rising dramatically. This is largely the result of production of new membranes for use in the RO process. These new membranes are much more chemically resistant and are capable of excluding smaller molecules.

A mobile, trailer-mounted, helicopter portable reverse osmosis unit has been constructed for Environment Canada by Memtek Corporation. The unit, which is entirely self-contained, is diesel powered and can produce up to 1800 litres per hour of pure water (permeate) from salt water. It is equipped with test points that make it possible to compare four separate membranes simultaneously.

A project has been started which will test four commercially available membranes against a series of dilute chemical solutions. These chemicals, which all come from the Environmental Emergencies Technology Division's list of problem spills, are representative of the various functional groups. As part of the project, the RO unit has been tested on leachate at a former chemical landfill in the Ottawa area.

THE PROBLEM

A glance at a map of Canada quickly reveals the large number of small water bodies present. Many more, too small to show on a map, occur along transportation rights-of-way in the form of ditches, ponds, sloughs and slowly flowing streams. An accident which results in a spill of a soluble chemical into one of these small bodies of water can present a severe problem. The result is many thousands of litres of a dilute chemical solution which may or may not be reactive but which must somehow be disposed of. Currently, the spill must be neutralized, if necessary, then the aqueous solution picked up, usually by vacuum truck, and transported to a location for recovery or disposal. Any technique which will reduce the volume of fluid to be removed and transported will lessen the problem. Reverse Osmosis appears to be such a technique.

REVERSE OSMOSIS

Osmosis is the process of diffusion of liquid, through a semipermeable membrane, from a region of low concentration to one of high concentration of solute. It is the process used in the growth of plants and operates at what is known as osmotic pressure (Figure 1). In reverse osmosis, the flow is reversed. An external force, usually but not always pressure, is exerted to overcome the osmotic pressure and the solute flows from the region of low concentration to that of high concentration (Figure 2). It is emphasized that this is a diffusion process, not one of filtration.

Reverse osmosis moved from the realm of a laboratory curiosity to practicality with the discovery of the Loeb-Sourirajan membrane. In these membranes, a very thin layer of a semipermeable material is deposited on a porous substructure (Figure 3). This provides a product with the strength necessary to withstand high pressures and with the short pathway necessary for high flow rates in a diffusion process.

The first membranes were made from cellulose acetate. This material is very satisfactory for the purpose for which reverse osmosis was first used on a large scale, the desalination of salt and brackish water. Cellulose acetate, and the first improvement upon it, cellulose triacetate, are also very capable of removing most inorganic salts and heavy metals from water. They are not, however, capable of removing small organic molecules. This is evidence that the process is one of diffusion, not filtration since cellulose acetate will block a small sodium chloride molecule (MW 58.5) but will pass a larger phenol molecule (MW 94.1). This deficiency, and the narrow pH range to which these materials may be subjected, has led to the search for better materials. Among those used are polyamides, polyimides, polyethers, polyesters and polysulphones. Each of these materials has advantages and disadvantages particularly in the range and classes of organic chemicals which it will either withstand or remove from water.

The field of membrane development is rapidly expanding and the latest membranes are thin-film composites, (Figure 4) utilizing a combination of the materials mentioned earlier. The form in which the membrane is used has also undergone much change in recent years. Many techniques to maximize flow rate while excluding as great a concentration of solute as possible have been tried.

There are, however, now three main configurations utilized in membrane elements. These are spiral wound (Figure 5), hollow fiber (Figure 6) and tubular (Figure 7). Each configuration has its advantages and disadvantages.

THE EPS MOBILE REVERSE OSMOSIS UNIT

Reverse osmosis is being investigated by EPS for two distinct purposes; the clean-up of chemical spills and the production of fresh water for steam clean-up of oil on low energy shorelines. The mobile unit was designed to carry out both of these functions. It is trailer mounted, helicopter portable and completely self-contained. It has its own diesel engine for power, DC and AC electrical generation and thermostatically controlled propane heating during storage. The capacity is 1800 liters of permeate (fresh water) per hour and this can be increased to 2400 litres per hour with minor modifications.

The unit layout is shown in Figure 8.

Operation of the unit is as follows:

a. the solution to be treated, either salt water or a spilled chemical is brought into the unit by the lift/feed pump: the pump is capable of providing solution at 380 L/m (100 US GPM) at a pressure of 960KPa (14 psig) when drawing from a depth of 10 metres;

b. the incoming solution is filtered through one of two banks of 10-25 micron filters designed to reduce fouling of the RO membranes by suspended solids;

c. the solution is passed through two high pressure pumps in parallel where the pressure is raised to 2750-6900 KPa (400-1000 psi) for reverse osmosis;

d. from the pumps, the solution is fed in parallel to two banks of three pressure vessels in series, each pressure vessel containing two reverse osmosis elements. These may be spiral wound, tubular or thin fiber elements. Only a minor plumbing change is required;

e. if the unit is being used to concentrate a chemical spill, the concentrate is fed back to the high pressure pump inlet in a recirculation loop designed to increase the chemical concentration to the desired level;

f. permeate (fresh water) and concentrate (solute and water) are discharged, the concentrate to a collection vessel and the permeate to any area away from the inlet source. There are test points on four of the permeate lines, making possible the testing four different membranes simultaneously.

The unit, once started, can be left unattended if necessary. Automatic controls are provided to ensure shut down in the event of:

a. normal pressures and temperatures are exceeded or not met;

b. blocked inlet; or

c. ruptured membrane (inorganic chemical only).

In addition, the selection of and change-over between filters is automatic with one filter unit or both being used depending on their condition.

THE REVERSE OSMOSIS EVALUATION PROJECT

As mentioned in the description of the unit, the EPS Mobile RO Unit has the capability to test four sets of two membrane elements simultaneously. This project makes use of that feature by evaluating four commercially available-membranes against representative chemicals from the EPS priority chemicals listing. For testing the unit plumbing is modified as shown in figure 10 to ensure that the feed seen by each membrane is the same.

The EPS priority chemicals list, of which you will hear more later, was developed because of the need to establish priorities to be investigated in the area of chemical spill clean-up. It is based on the chemicals that are most frequently transported and/or spilled in Canada, and their environmental impact if spilled. The "Top 50" are listed in Table 1.

The ability of reverse osmosis to remove a chemical from an aqueous solution is dependent on the membrane and also on the size of the molecule and the functional group. Within a given functional group (eg. alcohol, acid, alkali, ketone) the smaller the molecule, the more difficult it is to remove. This fact was considered when selecting the chemicals to be used in this study. The list, Table 2, comes almost exclusively from the "Top 50", the exceptions being 2,4-D, potassium hydroxide and calcium phosphate which come from the "Second 100". You will note that for the inorganic members, a different anion and cation is used in each instance. This provides a wide spectrum of ions. The list of test chemicals is thus considered to be very representative.

Selection of the membranes to be used in this project was done in consultation with the manufacturers. Letters were sent to all known manufacturers and Canadian suppliers explaining the purpose of the project and requesting data on the capability of their membranes, the cost, and the delivery times. From the responses received, a selection of the four most promising membranes was made. These were:

Manufacturer	Membrane	Membrane Material
TORAY	PEC 1000	TFC Polyether - Polysulphone
UOP	TFC 4600	TFC Polyether/amide - Polysulphone
FILM TEC	FT 30	TFC Polyamide/Polysulphone
DESALINATION INC	B 441	TFC Polyamide

* TFC is thin film composite

All of these membrane elements have a spiral wound configuration. This was not planned but occurred by chance.

Testing of the unit against the chemicals on the list will be carried out at the Memtek plant.

The test procedure is as follows:

a. 2000 liters of purified water will be prepared by reverse osmosis using UOP TFC Model 1001 membrane;

b. a solution strength shown in Table 3 will be prepared using the 2000 L and the applicable chemical;

c. the solution will be cycled through the RO unit for several hours to acclimate the membranes and ensure steady state conditions;

d. triplicate samples of feed, concentrate and permeate (one permeate for each membrane type) will be taken and analyzed; and

e. the concentrate recirculation will be adjusted and further samples taken and analyzed. This will provide information concerning the effect of chemical concentration on membrane performance.

Analysis of the samples will be by:

a. Gas chromatography for the organics;
b. Ion chromatography for fluoride and nitrate; and,
c. Atomic absorption for the other inorganics.

The objective of the test program will be to fill in the "Achieved" columns in Table 3.

As mentioned in the introduction, a portion of the test project involves use at the Gloucester Landfill in a test of leachate clean-up. The chemicals and concentrations involved in two test wells are as shown in Tables 12 and 13. To this listing must be added the humic acids normally found in soil and the many inorganic salts found in ground water in the region. The results of this testing, which is now complete, will be reported by Miss Aileen Larkin in a poster session.

SUMMARY

In summary, then, Reverse Osmosis is considered potentially to be a powerful tool in the arsenal of chemical spill clean-up methods. It is recognized that it is not a solution in itself since it only reduces the extent of the problem to be treated; it does not eliminate the problem completely. Nonetheless this is a step in the right direction.

A mobile reverse osmosis unit has been constructed. It has been demonstrated as a water purification device and the effectiveness of the various membranes is now being tested.

TABLE 1

LIST OF PRIORITY HAZARDOUS MATERIALS FOR THE ENVIRONMENTAL EMERGENCY BRANCH

The 50 Highest Priority Chemicals

(In Alphabetical Order)

Acetic Acid
Acetic Anhydride
Ammonia
Ammonium Nitrate
Ammonium Phosphates
Benzene
Butyraldehydes
Calcium Chloride
Calcium Oxide/Hydroxide
Carbon Dioxide
Chlorine
Cyclohexane
Ethylbenzene
Ethylene
Ethylene Dichloride (1,2-Dichloroethane)
Ethylene Glycol
Ethylene Oxide
Ferric Chloride
Formaldehyde
Hydrogen Chloride/Acid
Hydrogen Fluoride/Acid
Hydrogen Sulfide
Mercury
Methanol
Morpholine
Naphtha
Natural Gas
Nitric Acid
Phenol
Phosphoric Acid
Phosphorous
Potash (Potassium Chloride)
Propylene
Propylene Oxide
Sodium Chlorate
Sodium Chloride
Sodium Hydroxide
Sodium Hypochlorite
Sodium Sulfate
Styrene (Monomer)
Sulfur Dioxide
Sulfuric Acid (and Oleum)
Sulfur
Tetraethyl Lead
Toluene
Urea
Vinyl Chloride
Xylenes
Zinc Sulfate
2-Ethylhexanol

TABLE 2

Reverse Osmosis Testing-Chemical Selection

Functional Group	Chemical	Solubility	Solution Strength	Cleaning Solvents
Organic Acid	Acetic Acid	∞	1000 ppm	NA
Inorganic Acid	Hydrofluoric Acid	∞	1000 ppm	NA
Alkali	Potassium Hydroxide	1,070,000 ppm	1000 ppm	NA
Alcohol	Methanol	∞	1000 ppm	NA
Aromatic	Benzene	1,800 ppm	1000 ppm	Dilute Ethanol
Organic Oxide/Ether	Propylene Oxide	65,000 ppm	1000 ppm	NA
Organic Chloride	Ethylene Dichloride	8,700 ppm	1000 ppm	NA
Inorganic Chloride	Ferric Chloride	744,000 ppm	1000 ppm	NA
Aldehyde/Ketone	Formaldehyde	∞	1000 ppm	NA
Amide	Urea	780,000 ppm	1000 ppm	NA
Inorganic Nitrate	Ammonium Nitrate	1,920,000 ppm	1000 ppm	NA
Inorganic Phosphate	Calcuim Phosphate	300 ppm	100 ppm	Dilute HCl
Inorganic Sulphate	Zinc Sulphate	965,000 ppm	1000 ppm	NA
Chlorate	Soduim Chlorate	1,010,000 ppm	1000 ppm	NA
Pesticide	2,4,-D	900 ppm	500 ppm	Dilute Ethanol

TABLE 3

Reverse Osmosis Testing Results

Chemical	Toray PEC 1000		UOP TFC 4600		Film TEC FT30		DS1 B441	
	Expected	Achieved	Expected	Achieved	Expected	Achieved	Expected[1]	Achieved
Acetic Acid (1000 ppm)	>91%		>50%		>75%		N/K(P)	
Hydrofluoric Acid (1000 ppm)	N/K		>50%		<15%		N/K(G)	
Potassium Hydroxide (1000 ppm)	N/K		>50%		N/K		N/K(G)	
Methanol (1000 ppm)	>41%		>50%		>50%		N/K(S)	
Benzene (1000 ppm)	N/K		>50%		N/K		N/K(S)	
Propylene Oxide (1000 ppm)	N/K		>50%		N/K		N/K	
Ethylene Dichloride (1000 ppm)	N/K		>50%		N/K		N/K	
Ferric Chloride (1000 ppm)	N/K		>90%		>98%		N/K(G)	
Formaldehyde (1000 ppm)	>69%		N/K		>35%		N/K(S)	
Urea (1000 ppm)	>85%		>50%		>70%		N/K(P)	
Ammonium Nitrate (1000 ppm)	N/K		>90%		>90%		N/K(G)	
Calcium Phosphate (100 ppm)	N/K		>90%		>98%		N/K(G)	
Zinc Sulphate (1000 ppm)	N/K		>90%		>98%		N/K(G)	
Sodium Chlorate (1000 ppm)	N/K		N/K		>98%		N/K(D)	
2,4-D (500 ppm)	N/K		>90%		>98%		N/K(P)	

(1) DSI did not give percentage removals but used:

G - Good

S - Slight

P - Possible

D - May damage membrane

TABLE 4

GLOUCESTER LANDFILL ORGANIC CHEMICAL CONTAMINATION GTC WELL

CHEMICAL	CONCENTRATION (PPB)
1,1 - DICHLOROETHYLENE	8.5
TRANS 1,2 - DICHLOROETHYLENE	7.2
DIETHYL ETHER	500
1,1,1 - TRICHLOROETHANE	14
TETRAHYDROFURAN	160

TABLE 5

GLOUCESTER LANDFILL ORGANIC CHEMICAL CONTAMINATION

CHEMICAL WELL 36 W	CONCENTRATION (PPB)
DICHLOROMETHANE	578
ACETONE	2573
1,1 - DICHLOROETHYLENE	65
1,1 - DICHLOROETHANE	288
CHLOROFORM	4178
DIETHYL ETHER	736
1,2 - DICHLOROETHANE	258
1,1,1 - TRICHLOROETHANE	1002
CARBONTETRACHLORIDE	40
TRICHLOROETHYLENE	188
BENZENE	281
BROMOFORM	350
TETRACHLOROETHANE	TRACE
METHYL BENZENE	1
CHLOROBENZENE	1

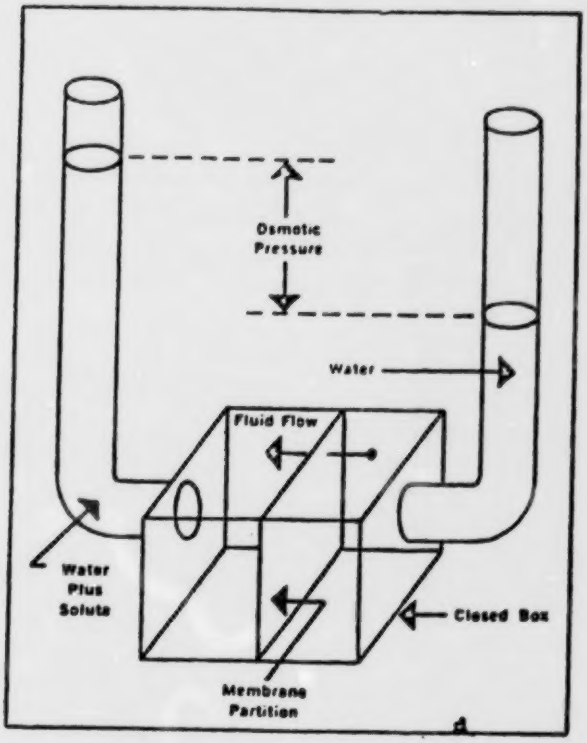

Osmotic
Pressure
Water
Fluid Flow
Water
Plus
Solute
Closed Box
Membrane
Partition

Figure 1. Osmosis

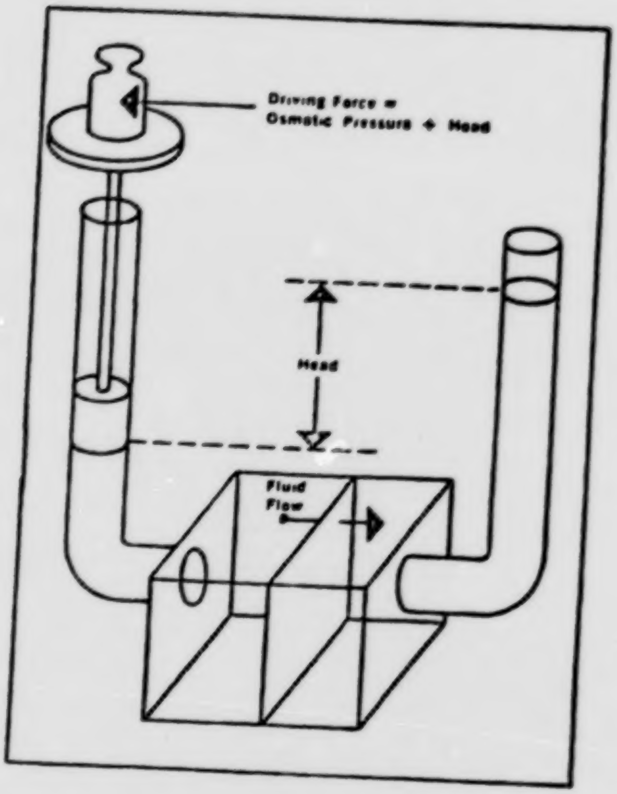
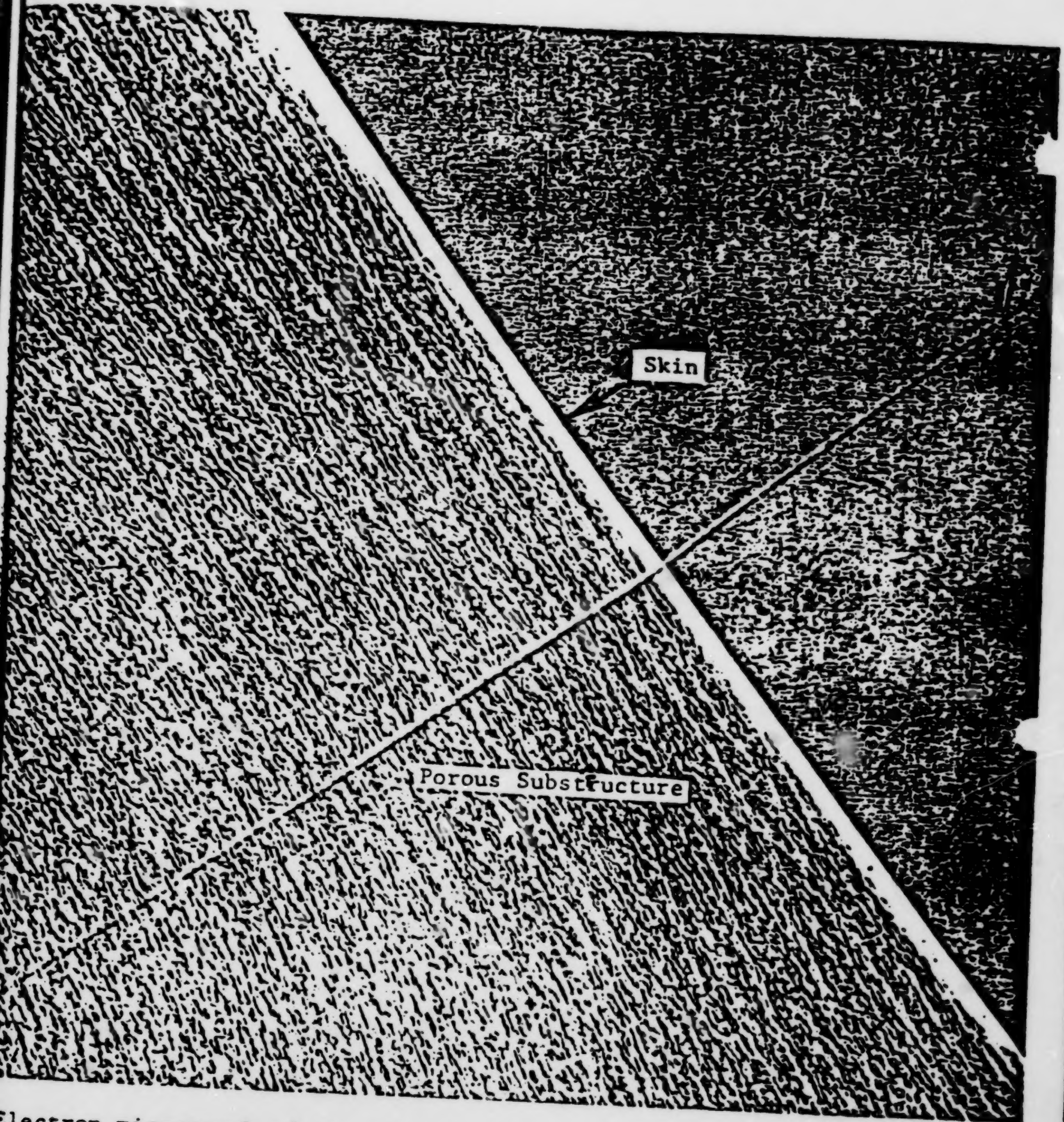

Driving Force =
Osmotic Pressure + Head
Head
Fluid
Flow

Figure 2. Reverse Osmosis

Figure 3.


Skin
Porous Substructure

Electron micrograph of the cross section of an anisotropic cellulose acetate membrane.

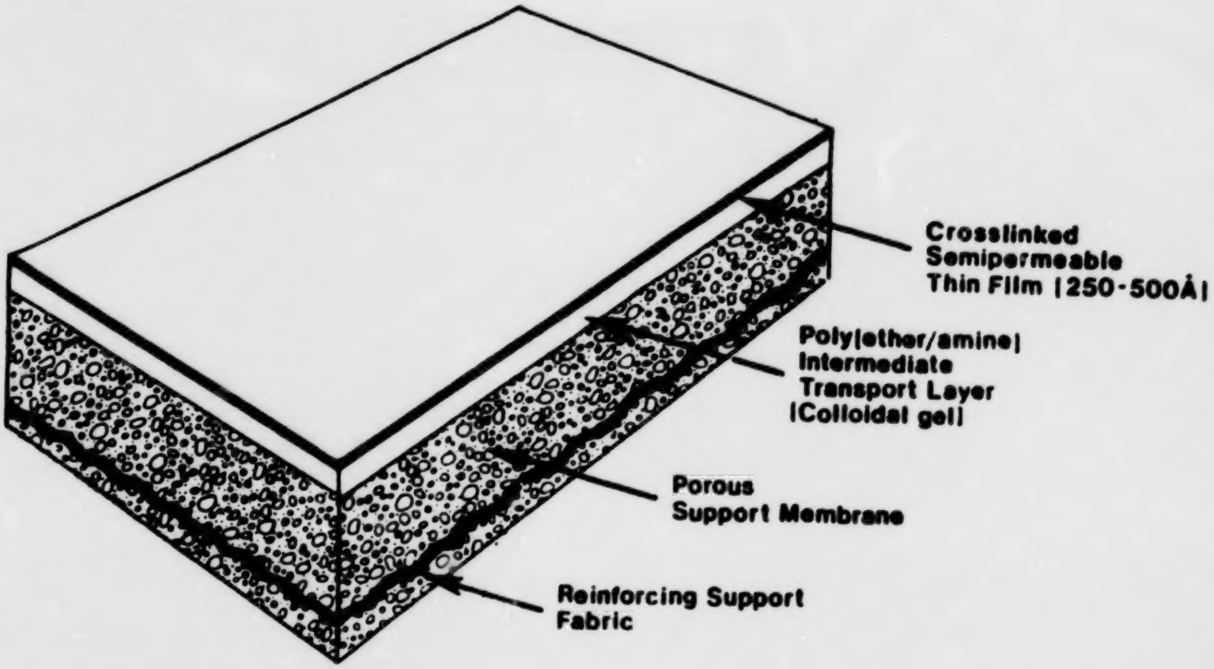

Crosslinked
Semipermeable
Thin Film (250-500Å)
Poly(ether/amine)
Intermediate
Transport Layer
(Colloidal gel)
Porous
Support Membrane
Reinforcing Support
Fabric

Figure 4. Cross sectional drawing of interfacially-formed thin-film composite membrane

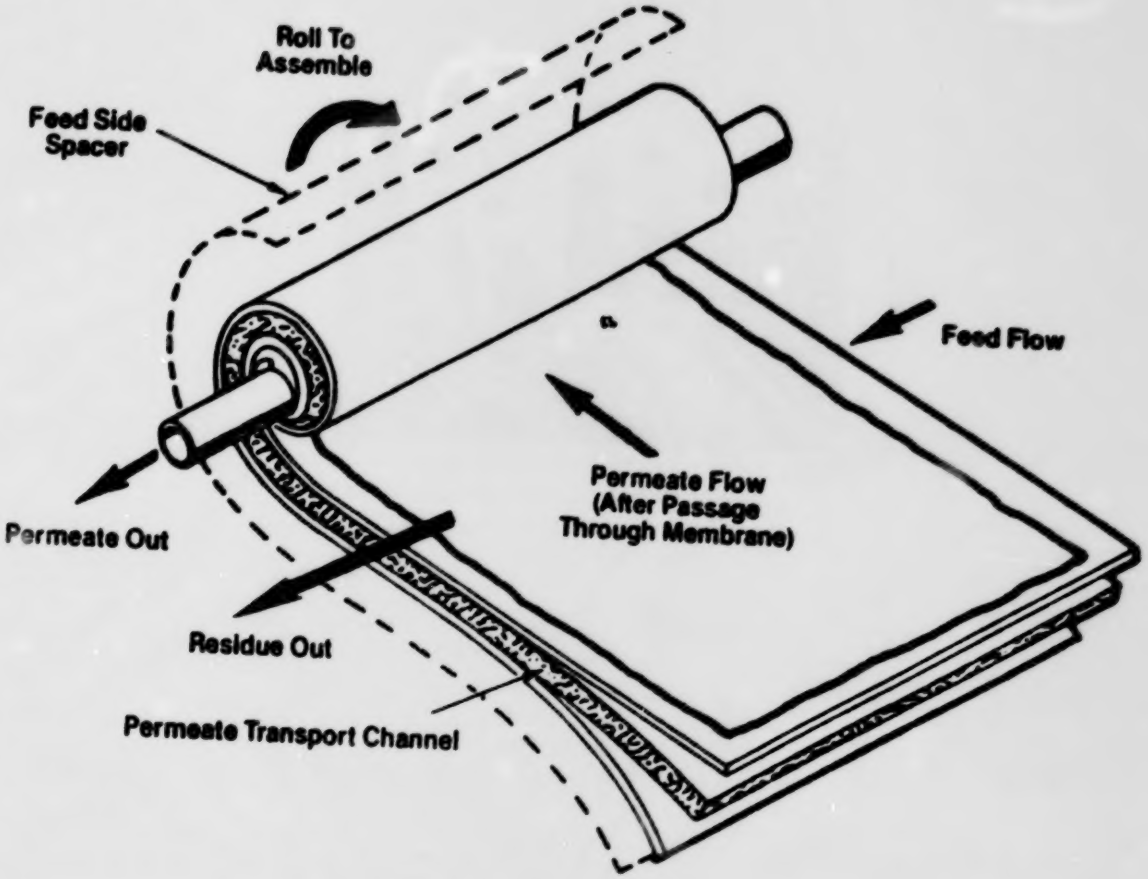
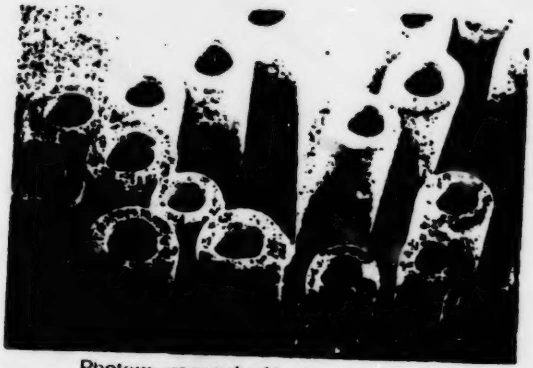
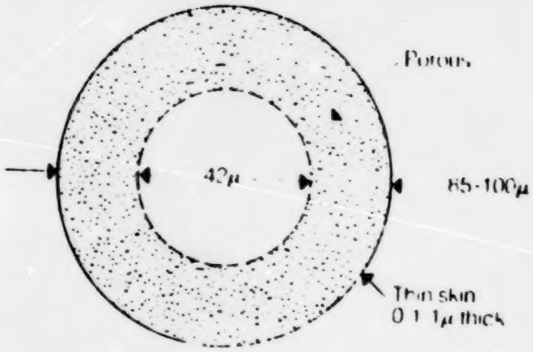

Roll To Assemble
Feed Side Spacer
Feed Flow
Permeate Flow (After Passage Through Membrane)
Permeate Out
Residue Out
Permeate Transport Channel

Figure 5. Spiral-Wound Element Construction



Photomicrograph of hollow fine fibers


Porous
42μ
85-100μ
Thin skin
0.1-1μ thick

1μ = micron = 0.00004 inch = 4/100,000 inch
42μ = 0.0016 inch   85μ = 0.0033 inch

Figure 6. Cross Section of Hollow Fiber (asymmetric aramid)

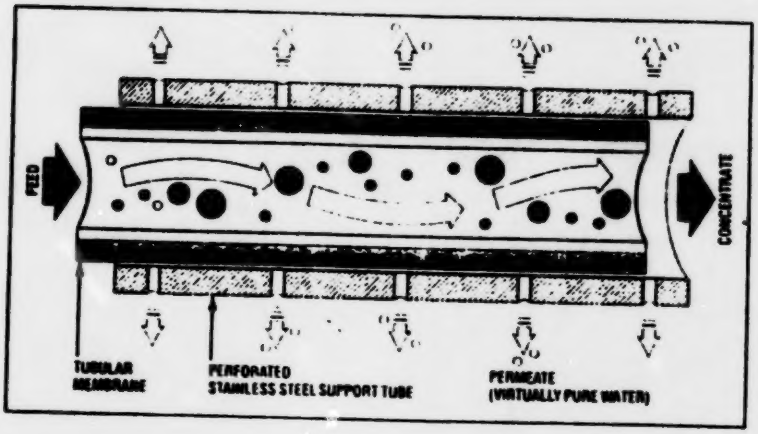
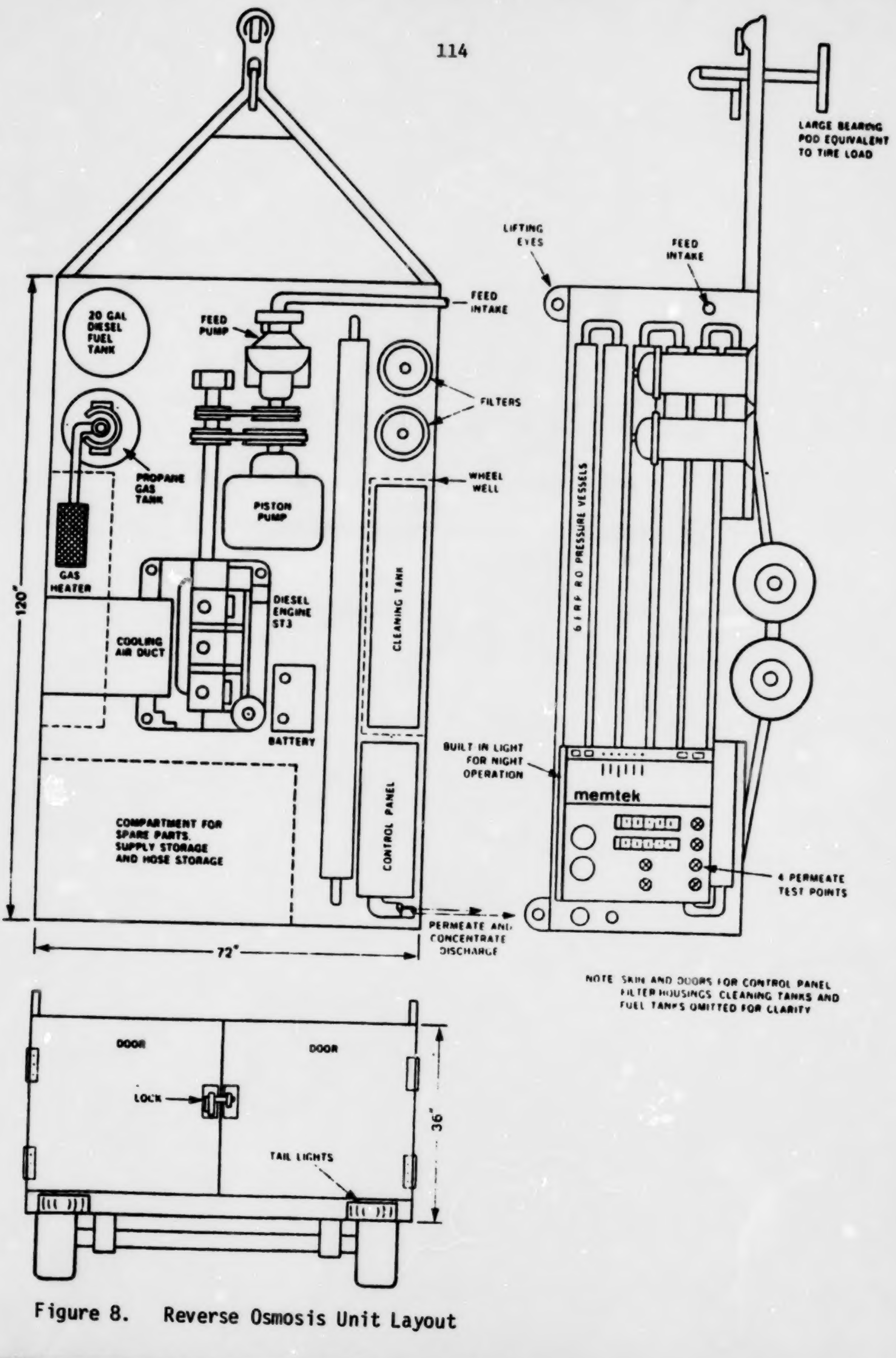

FEED
CONCENTRATE
TUBULAR MEMBRANE
PERFORATED STAINLESS STEEL SUPPORT TUBE
PERMEATE (VIRTUALLY PURE WATER)

Figure 7. Tubular Membrane


20 GAL DIESEL FUEL TANK
FEED PUMP
FEED INTAKE
FILTERS
PROPANE GAS TANK
PISTON PUMP
WHEEL WELL
GAS HEATER
COOLING AIR DUCT
DIESEL ENGINE ST3
CLEANING TANK
BATTERY
CONTROL PANEL
COMPARTMENT FOR SPARE PARTS, SUPPLY STORAGE AND HOSE STORAGE
120"
72"
PERMEATE AND CONCENTRATE DISCHARGE
LARGE BEARING PAD EQUIVALENT TO TIRE LOAD
LIFTING EYES
FEED INTAKE
6 F.R.P. RO PRESSURE VESSELS
BUILT IN LIGHT FOR NIGHT OPERATION
memtek
4 PERMEATE TEST POINTS
DOOR
DOOR
LOCK
TAIL LIGHTS
36"

NOTE SKIN AND DOORS FOR CONTROL PANEL FILTER HOUSINGS CLEANING TANKS AND FUEL TANKS OMITTED FOR CLARITY

Figure 8. Reverse Osmosis Unit Layout

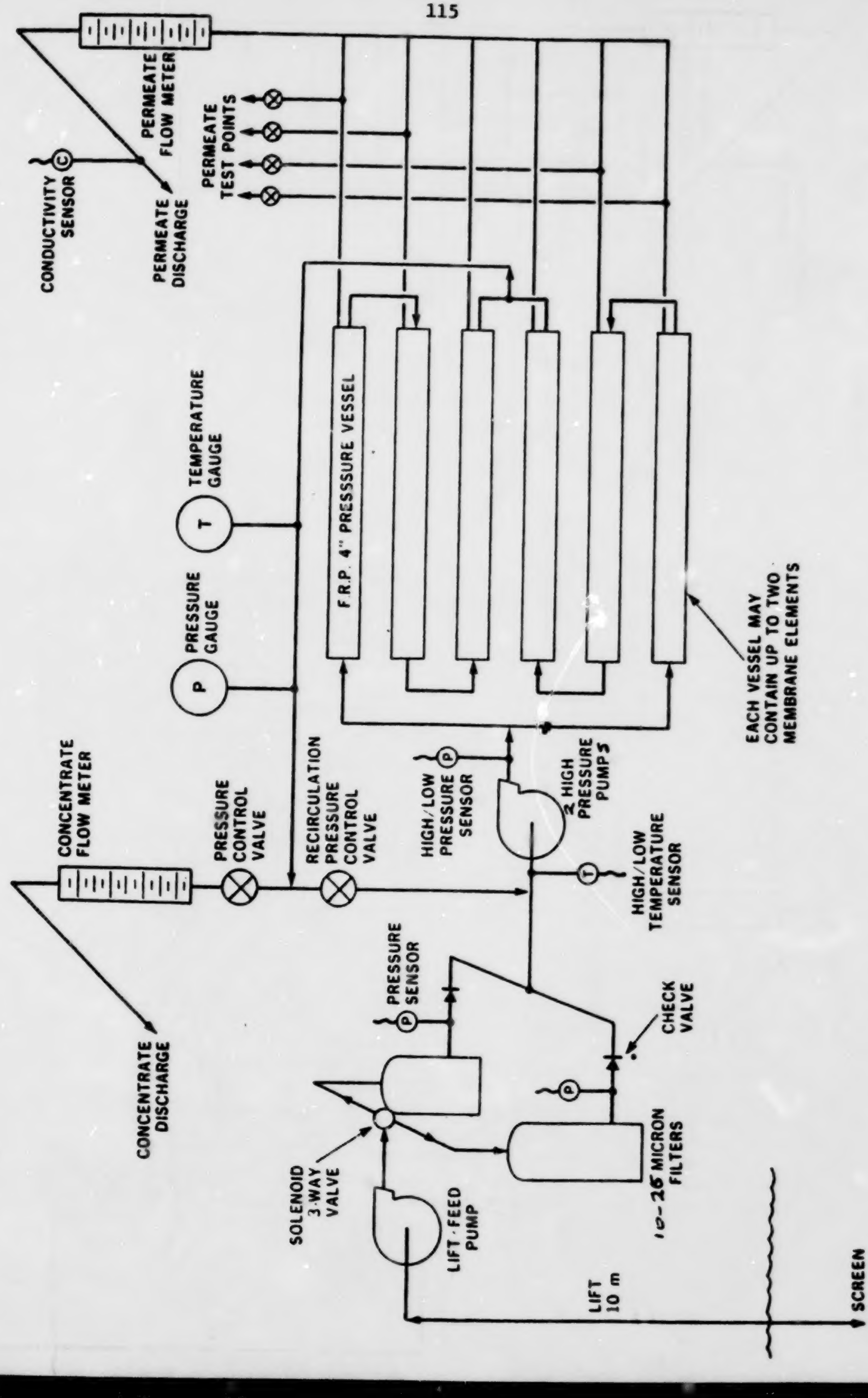

CONDUCTIVITY SENSOR
C
PERMEATE FLOW METER
PERMEATE DISCHARGE
PERMEATE TEST POINTS
CONCENTRATE DISCHARGE
CONCENTRATE FLOW METER
PRESSURE CONTROL VALVE
RECIRCULATION PRESSURE CONTROL VALVE
P
PRESSURE GAUGE
T
TEMPERATURE GAUGE
F.R.P. 4" PRESSSURE VESSEL
EACH VESSEL MAY CONTAIN UP TO TWO MEMBRANE ELEMENTS
HIGH/LOW PRESSURE SENSOR
2 HIGH PRESSURE PUMPS
HIGH/LOW TEMPERATURE SENSOR
PRESSURE SENSOR
CHECK VALVE
SOLENOID 3-WAY VALVE
LIFT-FEED PUMP
10-25 MICRON FILTERS
LIFT 10 m
SCREEN

Figure 9. Schematic of RO unit operation

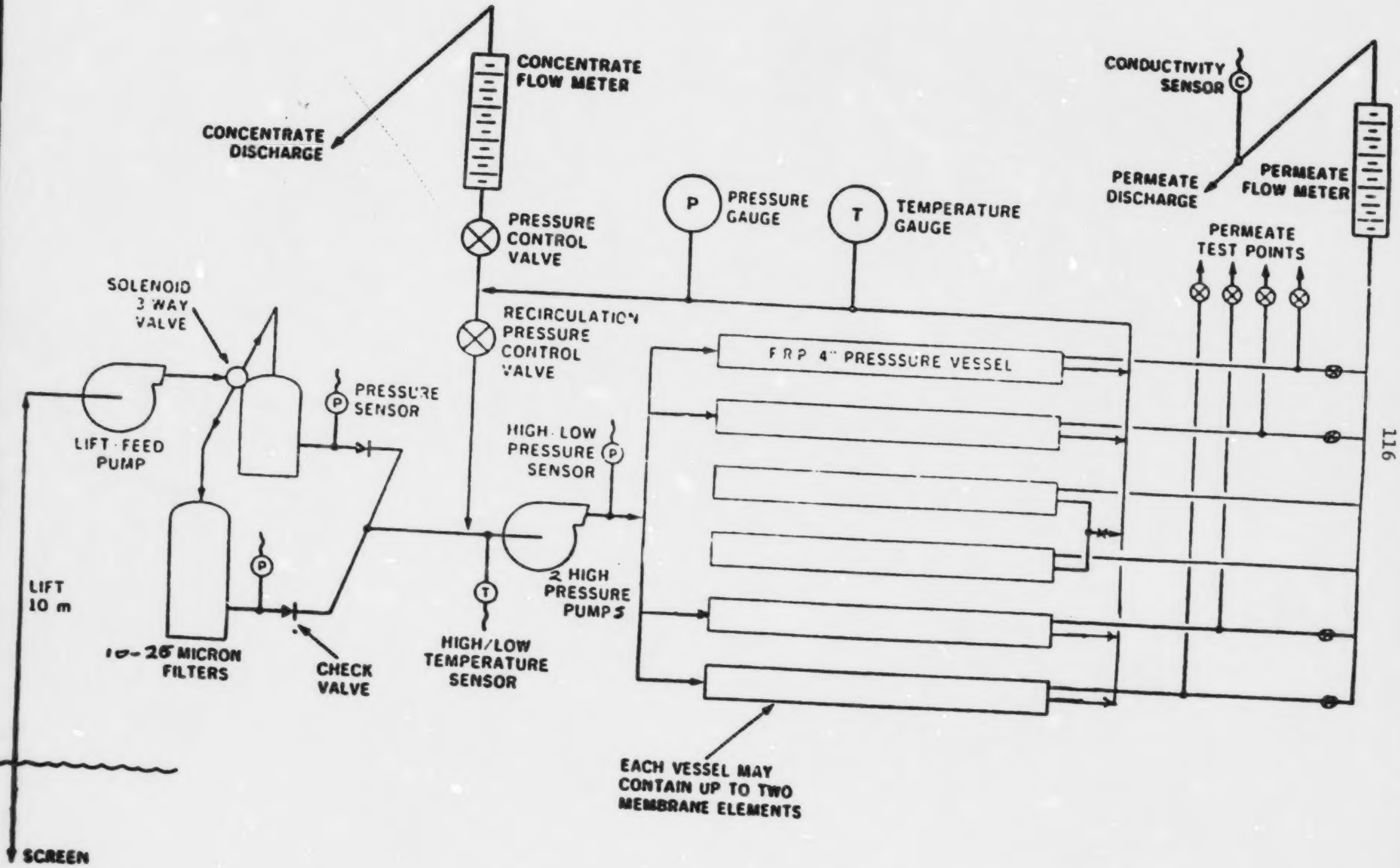

CONCENTRATE DISCHARGE
CONCENTRATE FLOW METER
PRESSURE CONTROL VALVE
RECIRCULATION PRESSURE CONTROL VALVE
P
PRESSURE GAUGE
T
TEMPERATURE GAUGE
CONDUCTIVITY SENSOR
C
PERMEATE DISCHARGE
PERMEATE FLOW METER
PERMEATE TEST POINTS
SOLENOID 3 WAY VALVE
LIFT FEED PUMP
PRESSURE SENSOR
HIGH LOW PRESSURE SENSOR
FRP 4" PRESSSURE VESSEL
LIFT 10 m
10-25 MICRON FILTERS
CHECK VALVE
HIGH/LOW TEMPERATURE SENSOR
2 HIGH PRESSURE PUMPS
EACH VESSEL MAY CONTAIN UP TO TWO MEMBRANE ELEMENTS
SCREEN

Figure 10. RO unit as reconfigured for testing

BIOLOGICAL SPILL CLEANUP*

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ABSTRACT

In situ biological cleanup following spills of biodegradable hazardous organic compounds in the soil/groundwater environment can be a cost-effective technique when proper engineering controls are applied. Biodegradation of hazardous organic contaminants by microorganisms can minimize liability by converting toxic reactants into harmless end products.

Two case histories are presented. The first case history describes land treatment techniques resulting in the removal of an estimated 730 kg of phenolic compounds in 1300 m^3 of soil initially contaminated with an estimated 820 kg of phenolics. Biological techniques provided more than a 30 percent cost savings over conventional transportation and disposal costs. The second describes subsurface-water cleanup of organic solvents.

KEYWORDS

Hazardous organic compounds, biological spill cleanup, biodegradation, total recoverable phenolics, land treatment techniques, industrial wastes, cometabolism, cosubstrate, underground recovery and treatment system, isopropanol, acetone.

INTRODUCTION

Biodegradation as a method for spill cleanup and environmental restoration is considered to be a promising technology (6, 34). Land treatment techniques have been engineered and are accepted as an economical and environmentally sound means of destruction for many types of industrial wastes (22, 25, 36). With regard to the cleanup of contaminated soil and groundwater, physical removal, by convention, has been the method of remediation. However, biological techniques are now gaining increasing acceptance as a practical, cost-effective method of cleanup.

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*Data in these case histories have been presented as "Biological Restoration of Soil and Groundwater" at the 1983 conference on Management of Leachate and Groundwater at Hazardous Waste Disposal Sites. Nashville, Tennessee; 1983 September 19-21.

Cleanups at 23 uncontrolled hazardous waste sites have resulted in costs ranging from $10 to $119/m^3 for excavation and from $1.22/liter for advanced oil/water separation to 0.00436 cents/liter for biodegradation (5). Biodegradation can offer many cost and technical advantages to environmental restorations. This paper identifies several advantages of biodegradation including cost-effectiveness, prevention of disturbance to operations, destruction of spilled compounds, and permanence of solution.

O.H. Materials Co. (OHM) has practiced biological cleanup of spilled substances since 1978 when a railroad incident resulted in spillage of acrylonitrile. Subsequent biological restoration projects have included additional acrylonitrile spills and other materials such as gasoline, crude oil, acetone, isopropanol, butyl cellosolve, ethyl acrylate, and several phenols.

Several factors must be considered before initiating a biological cleanup. The first consideration is to determine if the substrate is biodegradable in the environmental matrix. To accomplish this, OHM performs a bench-scale biofeasibility evaluation. Included in the evaluation is an assessment of methods to increase the degradation rate. Such methods commonly include use of surfactants, cosubstrates, vitamins, trace elements, etc. Toxicity of the environment to microbial growth is also assessed. The results of the biofeasibility evaluation form the basis for subsequent field implementation, as discussed in the following two case histories.

CASE HISTORY NO. 1: BIOLOGICAL DESTRUCTION OF PHENOLIC COMPOUNDS AT A USEPA SUPERFUND HAZARDOUS WASTE SITE USING LAND TREATMENT TECHNIQUES

Introduction

Biological techniques were successfully used to cost-effectively remove phenolic compounds from contaminated soil at the Picillo Farm, a USEPA superfund hazardous waste site in Coventry, Rhode Island. By the completion of the project, land treatment techniques resulted in the destruction of an estimated 730 kg of phenolics in 1300 m^3 of soil initially contaminated with an estimated 820 kg of phenolic compounds.

In the fall of 1977, an explosion and fire at the Picillo Farm led to the discovery of approximately 10,000 buried drums of hazardous wastes. In 1978, the Rhode Island Department of Environmental Management initiated a major clean-up effort at the Picillo Farm. A site investigation revealed there were four discrete trenches which contained buried drums. Beginning in the summer of 1980 and continuing through 1982, three discrete evacuation phases took place. During those phases 2300, 4500, and 3300 drums of hazardous wastes were excavated, sampled, analyzed, and composited for off-site disposal. The total cost of that operation exceeded three million dollars.

Approximately 1300 m^3 of hazardous soil remained on site. An initial analysis indicated the soil was highly contaminated with phenol and contained detectable levels of m-tert-butylphenol and p-1,1,3,3-tetramethylbutylphenol. The full spectrum of substituted phenolic compound contamination was not initially realized. For the purpose of evaluating more environmentally beneficial and cost-effective disposal options compared to secure landfill disposal, the Rhode Island Department of Environmental Management requested an approach for biodegrading the spill contaminants. The objective of the project was to reduce the total recoverable phenolics concentration to below 100 ppm.

Biodegradation potential of phenolic compounds has been well documented in the literature (7-11, 19, 29, 33). OHM had field experience in biodegrading phenol, o-chlorophenol, and pentachlorophenol. Therefore, there was a basis for initiating a biodegradation program at the Picillo site.

Biofeasibility Evaluation. Prior to initiation of the phenolics biodegradation feasibility study, the following screening analyses were performed on a composite of selected soil samples collected from the site: total recoverable phenolics, NH_3-N and PO_4-P nutrient concentrations, pH, microbial aerobic heterotroph populations, and percent moisture. Each of these parameters measures a unique aspect of the site matrix which must be understood and controlled for effective biological cleanup.

The analytical procedures used for sample analysis are summarized as follows:

1. Total Recoverable Phenolics. The soil samples were analyzed colorimetrically to quantify the total recoverable phenolics present using U.S. EPA procedures (Method 420.3, Total Recoverable Phenolics, Spectrophotometric, MBTH with Distillation) (35).
2. Inorganic Nitrogen and Ortho-Phosphate. Ammonia-nitrogen (NH_3-N) and phosphate-phosphorus (PO_4-P) were quantified spectrophotometrically by nesslerization and ascorbic acid, respectively (Hach Chemical Company, Ames, Iowa).
3. pH. Soil pH was determined for a soil-laboratory grade water slurry (1:1, wt/vol) with a calibrated pH meter.
4. Microbial Aerobic Heterotrophs. Bacterial enumeration was performed using standard plate count procedures (4). Samples were processed using membrane filtration techniques and standard plate count agar. Incubation was at 20 ± 1 °C for 48 ± 3 hours.
5. Percent Moisture. Moisture content was determined gravimetrically following drying to constant mass at 110°C in an oven. Moisture content was calculated as a percentage of the oven-dry weight of the soil (26).

Results of the screening analyses are presented in Table 1. Based on replicate analyses of the composite soil sample, the mean total recoverable phenolics concentration was 875 ppm. The soil contained a viable microbial population and had the inorganic nitrogen and phosphorus necessary to support an increased population. For effective cleanup, pH adjustment of the soil would be necessary.

TABLE 1 SCREENING ANALYSES PERFORMED FOR A COMPOSITE SOIL SAMPLE EVALUATED FOR TOTAL PHENOLICS BIODEGRADATION POTENTIAL.

TOTAL RECOVERABLE PHENOLICS (PPM)	NH_3-N (PPM)	PO_4-P (PPM)	pH	MICROBIAL AEROBIC HETEROTROPHS (CFU/g OVEN-DRY SOIL)	MOISTURE (%)
850	98	85	9.3	3.3×10^4	10.4
900	100	84		5.5×10^5	10.2
$\bar{x} = 875$	$\bar{x} = 98$	$\bar{x} = 84$		*G.M. = 1.4×10^5	$\bar{x} = 10.3$

*GEOMETRIC MEAN

The feasibility study was performed using the electrolytic respirometer (Exidyne Instrumentation Technologies, Inc., Colorado Springs, CO) which provided a direct and continuous measurement of oxygen uptake by microbial populations within six closed reaction vessels (with oxygen generated within the closed system). Oxygen uptake by microbial aerobic heterotrophs is a direct measurement of biodegradation taking place within the reaction mixture.

TABLE 2 EXPERIMENTAL DESIGN FOR ELECTROLYTIC RESPIROMETER BIODEGRADATION FEASIBILITY STUDY

VESSEL NUMBER	CONTENTS
	BIOLOGICAL AUGMENTATION
1, 2	SOIL SAMPLE + INOCULUM OF COMMERCIAL MICROBES
	INOCULUM CONTROL
3	INOCULUM OF COMMERCIAL MICROBES
	TOXICITY / INHIBITION CONTROL
4	SOIL SAMPLE + GLUCOSE
5	GLUCOSE + SOIL MICROBIAL INOCULUM
	ABIOTIC CONTROL
6	SOIL SAMPLE + $HgCl_2$ + KCN + NaN_3

With reference to Table 2, vessels 1 and 2 were replicates demonstrating the feasibility of biodegradation. Vessel 3 served as a control measuring oxygen uptake of the bacterial inoculum in vessels 1 and 2. Comparison of the rates of oxygen uptake in vessel 4 with vessel 5 demonstrates the presence of significant quantities of substances toxic or inhibitory to microbial growth. Nonbiological loss of the phenolic compounds was initially considered in vessel 6. Due to laboratory safety considerations, the recoverable phenolics were not quantified in the abiotic control; hydrogen cyanide would have been produced in an acidification step of the chemical procedure.

Respirometer vessels were prepared using procedures described by Young and Baumann (37). A suspension of Type R-5 microbes from Flow Laboratories, Inc. (Inglewood, CA) was prepared by mixing 18.0 grams of the dehydrated mixture in 750 ml BOD dilution water. The suspension was incubated with aeration for 5 hours at 20°C prior to inoculation in the respirometer vessels. Eight milliliters of the microbial suspension were added to respirometer vessels 1 through 3 after allowing the larger particulates to settle.

Glucose was added to a final concentration of 1.0 gram per liter in the toxicity/inhibition controls (i.e., vessels 4 and 5). The abiotic control (i.e., vessel 6) received the microbial poisons $HgCl_2$, KCN, and NaN_3 to respective final concentrations of 100, 320, and 320 mg/liter (21). A 50.0 gram (wet weight) soil sample was added to vessels 1, 2, 4 and 6. The microbial inoculum added to respirometer vessel 5 was composed of twenty-five milliliters of a 1% (wt/vol) soil suspension (10). The final volume in each of the one liter electrolytic respirometer vessels was brought to one liter with BOD dilution water. Stirring speed in each vessel was adjusted to maintain a three inch vortex.

Throughout the study, aliquots were periodically removed from respirometer vessels and were analyzed for pH and for NH_3-N, NO_3-N, and PO_4-P, which are sources of inorganic nitrogen and phosphorus to support microbial growth. When necessary, pH and inorganic nitrogen and phosphorus concentrations were adjusted to ensure that the chemical environment remained favorable for microbial growth.

Electrolytic respirometer oxygen uptake data for vessels 1 and 2 are presented in Figure 1. The ultimate BODs for respirometer vessels 1 and 2 were determined by subtracting the inoculum control (vessel 3) and fitting the corrected oxygen uptake data to a modified crescent curve:

$$y = a + be^{-kx},$$

where a = the ultimate amount of oxygen uptake to be expressed, y = the amount of BOD expressed or exerted at time x, and k = the rate constant (31). Ultimate BOD is defined as the total amount of oxygen required to degrade the organic matter present in a sample.

Table 3 presents degradation data for total recoverable phenolics. Based on an initial value of 875 ppm, respective reductions in vessels 1 and 2 were 36 and 66 percent. However, the ultimate BODs for both vessels were similar, indicating comparable total recoverable phenolics reductions could be expected.

TABLE 3 TOTAL RECOVERABLE PHENOLICS DEGRADATION IN REPLICATE ELECTROLYTIC RESPIROMETER VESSELS CONTAINING SOIL SAMPLES

	TOTAL RECOVERABLE PHENOLICS (PPM)		*REDUCTION (%)	BOD_L (PPM)	k (DAY^{-1})	r^2
	*DAY 0	DAY 6.5				
VESSEL 1	875	560	36	440	0.066	1.0
VESSEL 2	875	300	66	380	0.56	0.99

*MEAN OF REPLICATE ANALYSES

The soil environment appeared to be slightly stimulatory to microbial growth as evidenced by the slightly greater rate of oxygen uptake in the soil vessel compared to the control (Figure 2). At the termination of the study, initial oxygen uptake data in the toxicity/inhibition control (i.e.,

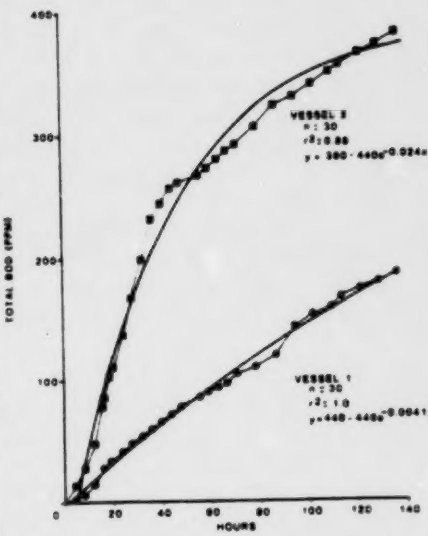

Figure 1 Feasibility Data electrolytic respirometer oxygen uptake data for replicate soil samples

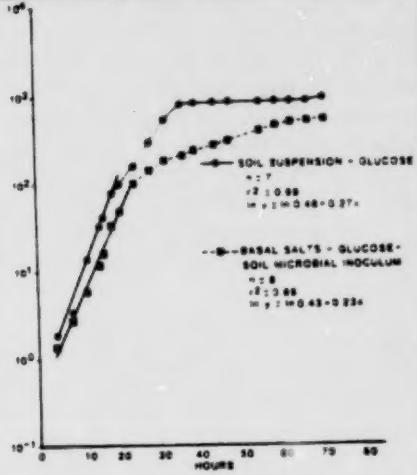

Figure 2 Toxicity / Inhibition Control electrolytic respirometer oxygen uptake data for a soil sample containing glucose and for a glucose control

respirometer vessels 4 and 5) were compared. On a semi-logarithmic plot, acomparison was made of the slopes of the lines-of-best-fit through the linear portion of the natural log transformed oxygen uptake data. In the linear portion of the semi-logarithmic plot the rate of oxygen uptake in the glucose-containing soil sample was 1.2 times greater than in the glucose control. Thus, evidence for an environment toxic or inhibitory to microbial growth was not found.

Evaluation of feasibility study results indicated that biodegradation techniques were a viable option to reducing the phenolics content of the soil. When compared to the other options that had been considered, such as secure landfill disposal, interceptor trenches, site encapsulation, etc., land treatment was more cost-effective. A land farming program was, therefore, initiated at the site.

Field Implementation. Figure 3 presents a treatment system schematic of the secured cell designed to prevent contaminant migration from the site. The control measures included a two-foot dike around the perimeter of the cell, two heat sealed impermeable visqueen liners separated by 15 cm of clean sand, a leach field consisting of perforated PVC pipe with a gravel pack, and a gravity-fed 190,000 liter bioreactor to collect and treat water for recirculation. The 1300 m^3 of sandy loam phenolics contaminated soil was farmed to an average depth of 46 cm in a 0.28 hectare-secured cell built for the land farming operation. Through frequent

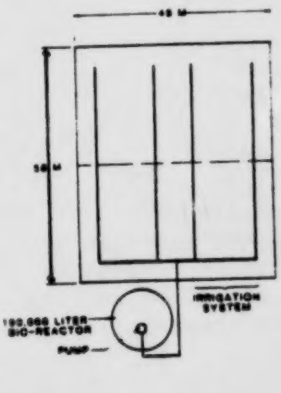

Figure 3 Treatment System Schematic

tilling, the soil was maintained in the loose condition necessary for the maintenance of aerobic conditions. For many compounds, greater rates of biodegradation generally occur in the aerobic environment. Maximum development of aerobic organisms takes place when the soil moisture content is about two-thirds of the water holding capacity (26). Moisture content was maintained within 60 to 80 percent of the moisture holding capacity of the soil with periodic pumping from the 190,000 liter bioreactor through the irrigation system. When inorganic nutrient concentrations and pH were within favorable ranges for bacterial growth and the soil had been tilled to provide good aeration, a mixture of commercially available bacterial strains were seeded into the soil to increase the microbial population density. A total of 350 pounds of the commercially available microbes were seeded into the treatment area during the 70-day operational phase with 100 pounds added within the first week of operation.

Throughout the project, sample collection was supervised by Rhode Island Department of Environmental Management personnel. On a weekly basis, eight soil cores were randomly collected from each of the four quadrants and a composit from each quadrant was analyzed for total recoverable phenolics, pH, inorganic nitrogen and phosphorus, percent moisture, and microbial aerobic heterotroph analyses. Based on the results of those analyses, environmental parameters were modified to maintain an effective rate of cleanup.

To determine the effect of tillage and continued addition of the commercially available bacterial strains on the rate of total recoverable phenolics degradation, a 2.3 m x 2.3 m x 0.46 m soil box control was constructed on day 13 and placed outside the treatment area and filled with soil taken from within the treatment area. Inorganic nitrogen and phosphorus nutrient concentrations and pH were within favorable levels for bacterial growth and remained within these levels for the remainder of the 70-day operation. No further nutrient or commercially available bacterial addition, pH adjustment, or tillage was made to the soil. Moisture content of the soil box control was maintained by frequent rainfall. Based on eight determinations made throughout its use, soil moisture content remained at 10.8 ± 1.5% (x ± s). Moisture content within the treatment area for the same time period was maintained at 12.3 ± 1.5% (n = 80). The control box also indicated the effect of cosubstrate addition initiated in week 6.

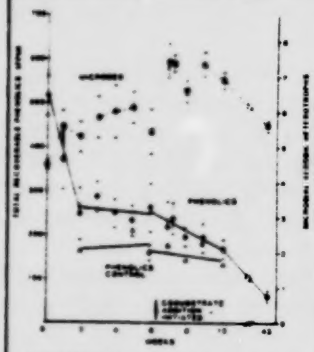

Figure 4 Field Data. Total recoverable phenolics and microbial aerobic heterotroph concentrations in the land farmed treatment area. The 95% confidence limits are presented for respective arithmetic and geometric means.

TABLE 4 REDUCTION RATES FOR TOTAL RECOVERABLE PHENOLICS

	REDUCTION RATE (PPM/WEEK)
LAND FARMED TREATMENT AERA	
DAY 0-13 (PHASE 1)	-150
DAY 13-41 (PHASE 2)	-3.7
DAY 41-70 (PHASE 3) COSUBSTRATE ADDITION	-2.1
SOIL BOX CONTROL	
DAY 13-41 (PHASE 2)	+0.43
DAY 41-70 (PHASE 3)	-0.70

Based on removal rates of total recoverable phenolics from the soil (Figure 4), field results were divided into three phases. In the land farmed treatment area, total recoverable phenolics reduction was rapid during the first phase (i.e., 13 days) of treatment with a weekly reduction rate in the soil approximately 150 ppm (Table 4).

The second phase of treatment (i.e., days 13-41) was marked by a significant reduction in the removal rate of the total recoverable phenolics in the soil. Reduction rates had changed from 150 ppm/week to 4 ppm/week. When the decreased rate of reduction was realized, the distillates used for total recoverable phenolics analyses were analyzed by GC procedures for USEPA priority pollutant phenolic compounds to determine if the samples initially analyzed were representative of the soil. GC procedures identified phenol, four chlorophenols (i.e., 2-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, and pentachlorophenol), two nitrophenols (i.e., 4-nitrophenol and 2,4-dinitrophenol), and 2,4-dimethylphenol. Thus, the soil had contained a heterogeneous mixture of phenolic compounds, and several of those compounds are not as readily biodegraded as phenol (33).

During this second phase, removal of 4 ppm/week was felt to be too low to quickly achieve the cleanup objective. It was decided to initiate addition of a cosubtrate to the treatment plot in order to increase the popultion density and activity of the biomass. Cosubstrates provide readily utilization sources of carbon and energy to support microbial growth. The results were immediate and dramatic indicating that cosubstrate addition is a powerful technique for enhancing biodegradation.

Cosubstrate addition initiated the third treatment phase and resulted in a six-fold increase in the rate of total recoverable phenolics removal which continued throughout the remainder of the treatment period. For cometabolized contaminants (1, 3, 13, 15, 18), addition of an appropriate cosubstrate can significantly increase degradation rate (12, 14, 16, 17, 28, 30). Cometabolism is defined as the oxidation of substances without utilization of the energy derived from the oxidation to support microbial growth (13). Although participation of cometabolism was not clearly demonstrated in this project, enhancement of the total recoverable phenolics degradation rate with cosubstrate addition implicates the existence of a cometabolic process in the system.

With below freezing temperatures on day 70, the practice of cosubstrate addition was terminated and that marked the end of the third phase of treatment. At that point, total recoverable phenolics concentration was only 68 ppm above the previously established objective of 100 ppm in the soil. On day 304, the mean total recoverable phenolics concentration in the treatment site soil was 61 mg/liter, a value significantly below the established goal for the project.

In situ destuction of the phenolic compounds in the soil environment using biological land treatment techniques provided an estimated cost benefit of $70,000 (representing a 30 percent savings) when compared to the cost of secure landfill disposal. This was based on estimated transportation and disposal costs of $230,000 and the actual job cost of $160,000. With biological treatment of greater soil volumes, proportionally greater cost benefits could be realized. In addition to the cost benefit achieved, future liability was minimized as a result of phenolics destruction in the on-site soil environment.

CASE HISTORY NO. 2: CLEANUP OF ISOPROPANOL-, ACETONE-, AND TETRAHYDROFURAN-CONTAMINATED SOIL AND GROUNDWATER

Introduction

The cleanup of subsurface waters containing isopropanol, acetone, and tetrahydrofuran by a combination of biological and physical techniques resulted in 90 percent removal of isopropanol and tetrahydrofuran within three weeks. The spill originated from several buried tanks which leaked contents into a shallow basin (3.7 m) containing 2800 m^3 of sand and pea gravel.

The initial problem was to determine if biological cleanup could be utilized to remove isopropanol and acetone; tetrahydrofuran was spilled in an early stage of the field operation. Acetone had not been spilled at the site but was suspected to be an incomplete oxidation product of isopropanol metabolism.

Isopropanol and acetone are biodegradable (32), therefore, there was a basis for initiating a biofeasibility evaluation.

Biofeasibility Evaluation. Results of analyses performed for soil and groundwater samples collected from the contaminated area and a clean control area are presented in Table 5. These data indicated that the values of all parameters were within favorable ranges for an enhanced biodegradation effort and only nitrogen and phosphorus needed to be augmented.

TABLE 5 SCREENING ANALYSES PERFORMED FOR SAMPLES COLLECTED WITHIN AND ADJACENT TO THE SPILL AREA PRIOR TO CLEANUP

	SOIL		GROUND WATER	
	SPILL SITE	CONTROL AREA	SPILL SITE	CONTROL AREA
ORGANICS (PPM)				
ISOPROPANOL			13	
ACETONE			13	
NUTRIENTS (PPM)				
NH_3-N			<0.20	
NO_3-N			<2.0	
PO_4-P			0.58	
MICROBES (CFU)	2.5 x 10^6/g	1.5 x 10^6/g	4.8 x 10^4/ml	1.3 x 10^5/ml
MOISTURE (%)	22.8	8.26		
pH			7.3	6.8

A biodegradation feasibility study was performed using static flask culture techniques (2,33). Isopropanol-acetone-basal salts media (500 ml per liter Erlenmeyer flask) were inoculated with 12.5 ml (10) of a 1% (wt/vol) soil suspension and incubated at ambient temperature. The soil used for the inoculum was a representative sample collected from the spill site. The medium employed contained 130 mg isopropanol, 60 mg acetone, 0.4 g KH_2PO_4, 1.6 g K_2HPO_4, 0.5 g NH_4NO_3, 0.2 g $MgSO_4 \cdot 7H_2O$, 0.025 g $CaCl_2 \cdot 2H_2O$, and 0.0025 g $FeCl_3 \cdot 6H_2O$ per liter laboratory grade water (15). The pH of the solution was adjusted to 7.2 with 1 N HCl or 1 N NaOH prior to inoculation. An uninoculated control was prepared to quantify nonbiological loss of isopropanol and acetone.

At periodic intervals throughout the study, aliquots were removed from the reaction mixtures and analyzed for pH and for isopropanol, acetone, NH_3-N, NO_3-N, and PO_4-P concentrations to ensure maintenance of a chemical environment favorable for bacterial growth. Isopropanol and acetone were quantified by headspace analysis on a Perkin-Elmer HS-6 unit (Perkin-Elmer Corporation, Instrument Division, Norwalk, CT) in conjunction with a Tracor 560 gas chromatograph (Tracor, Inc., Instrument Group, Austin, TX). The GC was equipped with a six foot 1% SP-1000 on 60/80 mesh Carbopack B column and with a flame ionization detector.

Figure 5 indicates that isopropanol was biodegraded stoichiometrically in the reaction vessel to acetone (32). This reaction was biological since it did not take place in the uninoculated control. Daily biological loss during the first eight days of the feasibility study was 5.8 mg/liter and nonbiological loss was 0.39 mg/liter. The concentration of acetone continued to increase until isopropanol was biodegraded to a trace amount and rapidly decreased once isopropanol was completely metabolized. The lack of a significant lag period indicated the presence of adapted, indigenous microbes which could biodegrade

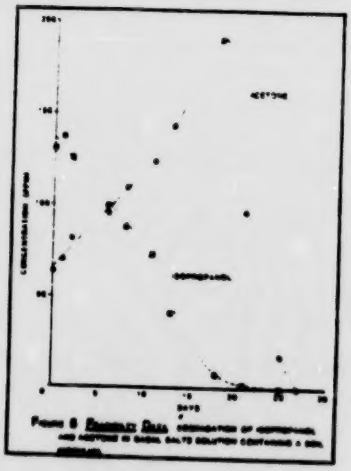

FIGURE 5 FEASIBILITY DATA. DEGRADATION OF ISOPROPANOL AND ACETONE IN BASAL SALTS SOLUTION CONTAINING A SOIL INOCULUM.

the contaminants. This finding was significant because it indicated that in situ biodegradation of isopropanol was already occurring and that OHM's management approach should be to increase the natural biodegradation rate.

A biodegradation feasibility study was not performed for THF since it was not an original contaminant. Published scientific literature describing the biodegradation potential of THF is not known.

Field Implementation. Use of the underground recovery and treatment system for aquifer restoration has been previously described (23, 24, and 27). For this project, the injection system was used to inoculate the underground environment with microbes capable of biodegrading the organic contaminants as well as provide the inorganic nitrogen and phosphorus necessary to support microbial growth. The recovery system was used to withdraw contaminated water from the ground for above ground treatment in an activated sludge treatment system. Effluent from the treatment system was reinjected into the subsurface environment creating a closed-loop system. Biodegradation of the spilled organic contaminants took place in the soil/groundwater environment as well as above ground in a biological treatment system.

Results in Figures 6-8 present respective isopropanol, acetone, and tetrahydrofuran concentrations over a 35 day period for recovery system effluent and for a centrally located test well. Patterns of concentration change for isopropanol and acetone were very similar. The spike on day 25 for the recovery system reflects the flushing of contamination pockets following repositioning of the injection/recovery wells. Comparison of Figures 6 and 7 support initial bench scale findings of biological conversion of isopropanol to acetone. After day 15, acetone concentrations continued to increase until a low concentration of isopropanol was reached and then decreased very rapidly. By day 38, acetone concentration was less than 2 mg/liter and by day 44 was below detection limits of 0.2 mg/liter.

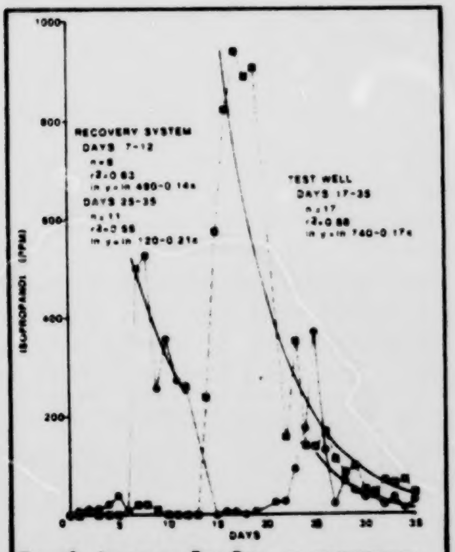

FIGURE 6 ISOPROPANOL FIELD DATA. IPA CONCENTRATIONS IN THE UNDERGROUND RECOVERY AND TREATMENT SYSTEM

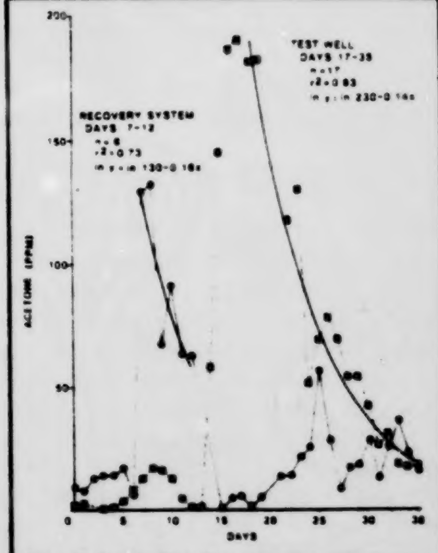

FIGURE 7 ACETONE FIELD DATA. ACETONE CONCENTRATIONS IN THE UNDERGROUND RECOVERY AND TREATMENT SYSTEM

Exponential decay curves were used to quantify removal rates of isopropanol, acetone, and THF from the groundwater environment. Holding other variables constant, the rates of decrease were assumed to be a function of contaminant concentration; i.e., $dy/dx = -by$, where y was the level of contaminant remaining, x was time, and b was the rate constant (20). The curves generated in that fashion were fit to a first-order equation of the form $y = ae^{-bx}$, where a was the concentration at time zero. The first-order rate constant, b, was determined by linear regression using least squares, and the first-order equation was converted to $\ln y = \ln a - bx$.

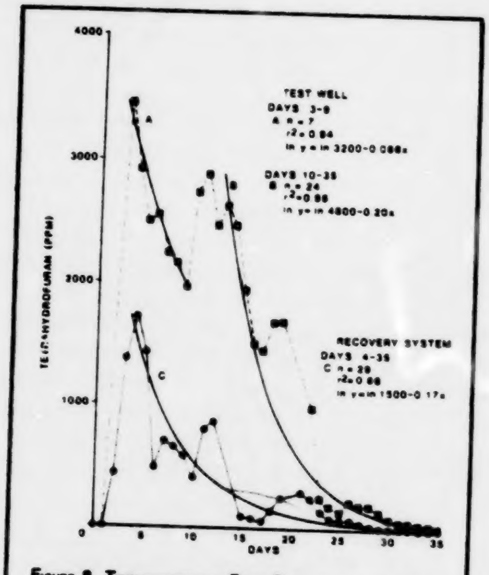

FIGURE 8. TETRAHYDROFURAN FIELD DATA. THF CONCENTRATIONS IN THE UNDERGROUND RECOVERY AND TREATMENT SYSTEM.

The calculated length of time for 50, 90, 95, and 99 percent removal of IPA, acetone, and THF from a test well and from the recovery system is presented in Table 6. Those rates reflect a combination of biological and physical removal. One line could not be fit to the data for each contaminant because physical changes in the injection/recovery system flushed out new pockets of contamination. Comparison of tetrahydrofuran test well data following adjustment of the injection/recovery system indicated that the calculated removal time was reduced by more than 50 percent.

Combination of physical and biological techniques were effective in removing these materials at a relatively rapid rate. The flexibility of the injection/recovery

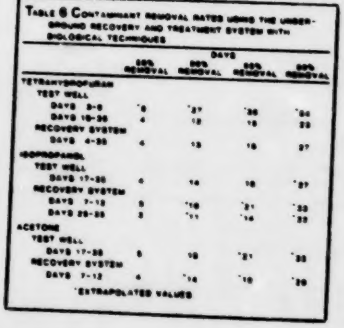

TABLE 6. CONTAMINANT REMOVAL RATES USING THE UNDERGROUND RECOVERY AND TREATMENT SYSTEM WITH BIOLOGICAL TECHNIQUES

	DAYS			
	50% REMOVAL	90% REMOVAL	95% REMOVAL	99% REMOVAL
TETRAHYDROFURAN				
TEST WELL				
DAYS 3-9	*8	*27	*35	*54
DAYS 10-35	4	12	15	23
RECOVERY SYSTEM				
DAYS 4-35	4	13	18	27
ISOPROPANOL				
TEST WELL				
DAYS 17-35	4	14	18	*27
RECOVERY SYSTEM				
DAYS 7-12	5	*16	*21	*33
DAYS 26-35	3	*11	*14	*22
ACETONE				
TEST WELL				
DAYS 17-35	5	16	*21	*33
RECOVERY SYSTEM				
DAYS 7-12	4	*14	*18	*28

*EXTRAPOLATED VALUES

system in innoculating the site with biological and flushing media was a key determinant in the removal of the scattered pockets of contamination.

DISCUSSION AND CONCLUSION

The two case histories demonstrate the potential of biological detoxification of contaminants in soil and aqueous environments. The data presented supports O.H. Materials Co. earlier work and findings on aquifer restoration using biological techniques. As discussed, biodegradation can offer substantial cost advantages over excavation, transportation, and disposal. The cost-savings range depends on the nature of the contaminant, extent of contamination, and distance from the spill site to an appropriate disposal facility.

Biofeasibility evaluation is an important first step in the implementation of a biodegradation program and should not be omitted. As currently practiced, the biofeasibility evaluation results in two catagories of information. The first catagory is the determination of whether a biodegradation program is feasible (biodegradation potential and toxicity limitations) and if so, what dilutions are required and what lag times can be expected. The second category is the identification of parameters managed via engineering controls. These parameters usually consist of pH, P, N, cosubstrates, etc. and affect the rate of biodegradation. As more is learned through the biofeasibility evaluation and subsequent field implementations, the biofeasibility evaluation will take on added importance as a predictive model for biological management.

A key area for future study is to determine the role of biological augmentation in biological cleanups. There is currently no scientific proof of the efficiency of commercial organisms vis-a-vis indigenous populations. We have found abundant populations of indigenous microorganisms, as described in case histories 1, 2, and other cleanups, and have demonstrated that they are capable of biodegrading the contaminants. Augmentation of commercial organisms to the spill site was implemented in both case histories described, but evidence is inconclusive that continued augmentation increases the rate of degradation. As indicated by our data, contaminants were removed from the spill sites by biological techniques.

The major determinant of effective spill cleanup using biological techniques is the application of proper engineering controls. For the two case histories, augmentation technology is critical to success. In the groundwater cleanup example, the ability to move the multiple injection points resulted in a more effective introduction of media than if a single injection point had been used. The land treatment of phenolics was enhanced by scheduled tilling and augmentation. The success of the cosubstrate ammendment was dependent upon management of the method, type, and rate of application.

The second case history demonstrates the effectiveness of combining physical recovery with biodegradation in the subsurface-water environment. Although we cannot identify the specific roles of biodegradation and physical recovery, we feel that comparison of laboratory and field data indicate that rates of reduction are similar.

As these case histories indicate, biological degradation can be useful and cost-effective in spill cleanup. Field implementation, however, is dependent upon understanding the biodegradation process and the ability to make the system work in the soil and groundwater environment.

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A SURVEY OF CHEMICAL SPILL COUNTERMEASURES: PRELIMINARY FINDINGS

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SURVEY DESCRIPTION

In 1980, the Environmental Protection Service (EPS) initiated a study to survey countermeasures suited for the control of hazardous material spills. The work was completed and published in 1982 as a draft report (Dillon, 1982). In 1983, EPS decided to complete this survey by updating it, expanding it, and verifying the contents.

The prime objective of the survey is to provide a ready source of information on countermeasures equipment and materials for those researching or planning purchase of spill control technology. A secondary, related purpose is to allow developers of countermeasures to assess current capability and thus direct their efforts to fulfilling the greatest needs and avoiding duplication of effort.

The data originate from an extensive survey of industry, government and private organizations involved in the development, manufacture or use of such systems. Information was and is now being solicited from sources around the world, the primary source being North America. It is, in fact, important that the survey be updated periodically since the field of chemical spill control equipment is a relatively new and rapidly developing one. As part of the revision process, it was felt that the 1982 survey would best be circulated as a draft document in order to obtain comments, corrections and additions for the compilation of a comprehensive and practical first report. This would then form a sound basis for accommodating new product information, evolving concepts, and changing priority spill substances.

The listing of equipment, systems and materials has been developed using the following classification system:

1. containment
2. mechanical recovery
3. transfer systems
4. temporary storage
5. handling devices
6. treatment

This system is further elaborated upon in Table 1. The classification scheme was derived from an analysis of those items presented in the original survey and, it is believed, reflects equipment that is actually available.

The survey does not include a number of items which may have relevance to chemical spills, including hardware suited to oil spills. Oil spills are not considered to be hazardous materials for the purposes of this survey. Also, equipment not directly related to chemical spill control is not included. For example, personnel protection gear and detection devices have been catalogued elsewhere (Buchan, 1981 and Dick, 1981). In addition to these exclusions, it was noted that some oil spill equipment such as booms, vacuum trucks and skimmers will, in the future, be included only as "group listings" rather than according to individual manufacturers. In the case of oil spill skimmers, a catalogue has already been compiled (Solsberg, 1982). A similar catalogue is being prepared for oil spill booms.

Table 1. CLASSIFICATION SCHEME FOR EQUIPMENT IN THE SURVEY OF COUNTERMEASURES

1. Containment
    - 1.1 Leak Plugging
    - 1.2 Land Containment
    - 1.3 Containment of Spills on Water
    - 1.4 Containment of Spills in Water
    - 1.5 Vapour Suppression

2. Mechanical Recovery
    - 2.1 Recovery from Land
    - 2.2 Recovery from Water - Floating Materials
    - 2.3 Recovery from Water - Sinking Materials

3. Transfer Systems
    - 3.1 Transfer of Gases
    - 3.2 Pumps for Liquids
    - 3.3 Transfer Hoses
    - 3.4 Transfer of Multi-state Materials

4. Temporary Storage

5. Handling Devices

6. Treatment
    - A. Systems or Processes
        - 6.1 Incineration
        - 6.2 Chemical/Physical Modification
        - 6.3 Removal from Water
        - 6.4 Removal from Soil
    - B. Agents
        - 6.5 Chemical Modification Agents
        - 6.6 Sorbents
        - 6.7 Gelling Agents
        - 6.8 Precipitating/Flocculating Agents
        - 6.9 Biological Agents
    - C. Applicators
        - 6.10 Treating Agent Applicators

Each data sheet or listing consists of a synopsis of the equipment's physical and operating characteristics, with sources specified for obtaining additional information. The following data are provided:

- description
- operating principle
- physical specifications
- operating specifications
- performance data
- usage
- availability and commercial information

ASSESSMENT

In addition to providing equipment listings, the survey provides summary or assessment tables. These allow a user to verify capability for a specific substance included in the EPS priority list. In addition, the substances are divided into groups based on physical/chemical properties, allowing one to generally choose countermeasures for a group, given that materials compatibility is verified.

These summary tables can be used to assess the current state-of-the-art in chemical spill countermeasures as illustrated in Table 2. This tabular assessment was prepared after completion of the original survey to summarize the potential of existing countermeasures to control various groups of chemicals. It should be noted that this is an assessment of potential rather than actual capability. On the basis of this type of assessment, EPS has stated that its priorities of countermeasures development are:

- removal of soluble materials from water
- vapour control
- removal of sinking materials from water
- removal of all chemicals from soil

EPS has already initiated development studies on the first two items.

Additionally, such analysis provides a summary of testing and evaluation requirements. Based on the first survey, it has been found, for example, that for the chemicals on the EPS priority list, only 0.3% of the countermeasures have been tested and only 0.1% (one out of a thousand) have had use documented on a spill of that substance. Thus it would appear that further evaluation and assessment work is needed. These results also underline that the survey now establishes potential applicability of countermeasures and not actual response capability.

CONCLUSIONS

The survey of countermeasures systems is in the process of being updated, revised and expanded to include all known devices or materials which can be used to control a chemical spill. The resulting manual will be useful to potential buyers as well as to those developing countermeasures. This update will be completed by the summer of 1984 and should be available in hard copy by the fall of that year. Work performed to date has served to indicate specific research priorities as well as a requirement to evaluate potentially useful countermeasures systems.

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Table 2. ASSESSMENT OF CHEMICAL SPILL COUNTERMEASURES POTENTIAL
(Higher Values Indicate Greater Potential, See Key Below for the Rating System)

Countermeasures Type	Sinking Soluble Solids	Insoluble Sinking Solids	Liquids That Mix	Sinking and Immiscible Liquids	Floating and Immiscible Liquids	Gases	Overall Potential Average
Containment							
Leak Plugging	[1]	NA	1	3/4	1	¼	0.8
Land Containment	1	[NA]	1	3/4	3/4	NA	0.9
On Water	NA	NA	NA	NA	1	NA	1
In Water	1	½	3/4	3/4	NA	NA	0.8
Vapour Suppression	NA	NA	NA	NA	[½]	½*	0.5*
Mechanical Recovery							
From Land	NA	1	1	1	1	NA	1
From Water - Floating	NA	NA	NA	NA	1*	NA	1*
From Water - Sinking	NA	3/4*	NA	¼*	NA	NA	0.5*
Transfer Systems							
Gases	NA	NA	NA	NA	NA	¼	0.3
Pumps	1	[1]	3/4	[½]	1	NA	0.9
Hoses	1	[1]	1	1	½	½	0.8
Multi-state	½	½	0	0	½	[0]	0.3
Temporary Storage	1	¼	¼	0	¼	[0]	0.4
Handling Devices	½	½	0	0	0	0	0.2
Treatment							
(a) Systems							
Incineration	¼	3/4	¼	½	3/4	0	0.4
Chem/Phys. Modification	½	½	½	½	3/4	0	0.5
Removal from Water	½*	[½]	½*	[½]	[¼]	NA	0.5*
Removal from Soil	0	0	0	0	0	NA	0
(b) Agents							
Chemical Modification	0	½	0	0	0	0	0.1
Sorbents	1	¼	3/4	3/4	1	NA	0.8
Gelling	½	¼	½	½	½	NA	0.5
Precipitating	0	NA	0	0	NA	NA	0
Biodegrading	0	0	0	0	½	NA	0.1
(c) Applicators	0	NA	0	0	NA	NA	0
Overall Average	0.5	0.5	0.4	0.4	0.6	0.2	0.4

Legend Assessment:

0 - no potential for development or commercialization
¼ - only one possibility for development
½ - two potential countermeasures
3/4 - three potential countermeasures
1 - countermeasures potential for most substances

[ ] brackets indicate conditional applicability
* indicates countermeasures deemed to be important for euvironmental control

U.S. EPA, OERR's SUMMARY OF SEPTEMBER 1982 INTERIM STANDARD OPERATING SAFETY GUIDES

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INTRODUCTION

The Environmental Response Team (ERT) is the Environmental Protection Agency's focal point for technical assistance to the Regions and program offices during single or multimedia emergency episodes involving toxic and hazardous materials. When activated by EPA Headquarters, Regional Offices, or Federal/State departments outside EPA, the ERT will provide assistance concerning prevention, safety, assessment, containment, control cleanup, restoration, removal, and disposal of oil and hazardous substances spills. Response activities include providing advice and consultation as well as conceiving, implementing, and coordinating novel and advanced technical approaches for solving problems associated with multimedia environmental emergencies such as chemical spills.

The September 1982, "Interim Standard Operating Safety Guides" are not meant to be a comprehensive safety and occupational health manual for incident response. Rather, it provides additional guidance on safety and occupational health to complement professional judgement and experience, and to supplement existing safety criteria. This paper is an overview of safety procedures and operations used at hazardous chemical spills and toxic waste sites responses as presented in the September 1982 Guides. The Guides are a revision of the April 1981 "Interim Standard Operating Procedures" which were initially developed by ERT to provide safety procedures for hazardous waste responses. Although every endeavor on or off-site involves some degree of consideration for worker protection and safety, this document outlines specific criteria for standard operating procedures primarily related to site control and entry. The omission of other safety procedures does not imply their lack of importance.

The following phases are addressed in the September 1982 "Interim Standard Operating Safety Guides":

Part 1 - Environmental Incidents
Part 2 - Standard Procedures
Part 3 - General Measures and Requirements
Part 4 - Site Entry - Survey and Reconnaissance
Part 5 - Site Entry - Levels of Protection
Part 6 - Site Control - Work Zones

Part 7 - Site Control - Decontamination
Part 8 - Air Monitoring (To be completed)

A major consideration in all response activities is the health and safety of the personnel. Not only must a variety of technical tasks be conducted in a timely fashion, but they must be accomplished in a manner to protect the worker. In addition to having appropriate equipment and training, safety-oriented standard operating procedures provide another means of reducing the possibility of harm. ERT has developed and offers eight training courses designed for field response and operations personnel who are expected to function in hazardous chemical environments. These courses are:

1.	Personnel Protection and Safety, 165.2	(5 days)
2.	Incident Mitigation and Treatment Methods, 165.3	(5 days)
3.	Sampling at Hazardous Materials Incident, 165.9	(3 days)
4.	Hazardous Materials Incident Response Operations, 165.5	(5 days)
5.	Hazard Evaluation & Environmental Assessment, 165.6	(5 days)
6.	Hazardous Waste Site Inspections, 165.10	(5 days)
7.	Response Safety Decision-Making Workshop, 165.8	(5 days)
8.	Air Monitoring - At Hazardous Materials Incidents, 165.4	(4 days)

Further course information may be obtained by contacting: Thomas C. Sell, Training Coordinator, Environmental Response Team, U.S. Environmental Protection Agency, 26 West St. Clair, Cincinnati, Ohio 45268, (513) 684-7537

HAZARD IDENTIFICATION

Characterizing a hazardous substance incident is generally a two phase process. The first phase is an initial or preliminary evaluation based on information that is readily available and/or the fairly rapid collection of data needed to determine if emergency protective measures are neccessary. The second phase of characterization, if needed for the incident, is more of a traditional environmental survey designed to enhance, refine, and enlarge the initial data base.

The purpose of an evaluation is to establish a plan of action for mitigation and treatment of the site and protection of those persons in contact with the hazard during such operations. Protection from chemicals comes in the form of protective clothing and respiratory protection apparatus. The question arises, how much protection is necessary? Speculative guessing is not the best way to choose the proper equipment. Thus, we must use those guidelines which are the most suitable to our needs. The source of such guidelines come from Federal/State regulations, Federal recommendations, and private organizations.

The objective of using total atmospheric gas/vapor concentrations for determining the appropriate personnel protection level is to provide a numerical criteria for selecting level A, B, or C protection. Until atmospheric contaminants are specifically identified and personnel protection selected based on toxicological properties, total gas/vapor concentrations provide a numerical value that can be used as a guide for selecting personnel protection equipment.

Although total gas/vapor concentration measurements are useful to a qualified professional for the selection of protective equipment, caution should be used in the interpretation of this data. The response of an instrument to several gas/vapor contaminants does not provide the same sensitivity as measurements involving a single contaminant. Since total vapor field instruments see all contaminants in relation to a specific calibration gas, the concentration of an unknown environment may be overestimated or underestimated.

When carcinogens or other highly hazardous substances are suspected, the protection level should not be based solely on the total gas/vapor criteria, rather the level should be selected on a case-per-case basis weighing heavily on potential exposure and chemical characteristics of the suspected material.

In utilizing atmospheric gas/vapor concentrations as a guide for selecting a level of protection, a number of factors should be considered:

1. The uses, limitations, and operating characterisitics of the monitoring instruments must be recognized and understood. Instruments such as the photoionizer (PID) and Organic Vapor Analyzer (OVA) do not respond to all substances that may be present or may respond differently to identical substances when compared to one another. Therefore, experience, knowledge, and good judgement must be used to complement the data obtained with this instrumentation.

2. Hazards, other than detectable toxic gases/vapors such as non-detectable gases (i.e., phosgene, hydrogen cyanide, chlorine, etc.,) liquid/solid particulates, explosives, combustibles, radiation, oxygen deficiency, and other harmful conditions may exist in the atmosphere or on the site.

3. The risk to personnel entering an area must be evaluated against the need for entering. Although this assessment is largely a value judgement, a conscientious deliberation of the variables involved and the risk to personnel must be balanced against this need for site entry.

4. The knowledge that carcinogens or other highly toxic substances are involved or suspected, requires that gross levels not be

the sole factor in determining the level of protection. Other factors which must be taken into consideration are exposure, chemical characteristics of known/suspected materials, instruments, weather conditions, etc.

5. Functions which need to be performed on-site must be evaluated. Based upon total atmospheric gas/vapor concentrations, level C protection may be judged adequate. The work functions to be performed such as moving drums, opening containers, bulking of materials, and other operations that increase the probability of exposure, may require a higher level of protection.

RESPIRATORY AND PERSONNEL PROTECTION SELECTION CRITERIA

It is important that personnel protective equipment and safety requirements be appropriate to protect against the potential or known hazards at an incident. Protective equipment should be selected based on the types, concentrations, possibilities, and routes of personnel exposure from substances at a site. In situations where the type of materials and possibilities of contact are unknown or the hazards are not clearly identifiable, a more subjective determination must be made of the personnel protective equipment required for initial safety.

The appropriate level of protection shall be determined prior to the initial entry on-site based on best available information. Subsequent information may suggest changes in the original level selected.

Levels of Protection

Level A - 500-1000 ppm Gas/Vapor Concentration Above Background

Level A protection should be worn when the highest available level of respiratory, skin, and eye contact protection is needed. While Level A provides maximum available protection, it does not protect against all possible airborne or splash hazards. For example, suit material may be rapidly permeable to certain chemicals in high air concentrations or heavy splashes.

Level B - 5-500 ppm Gas/Vapor Concentration Above Background

Level B protection should be selected when the highest level of respiratory protection is needed, but exposure to the small unprotected area of the body (i.e., neck) is unlikely, or where concentrations are known to be within acceptable exposure standards.

Level B protection is the minimum level recommended on initial entries until the hazards have been further identified and defined by monitoring, sampling, and other reliable methods of analysis, and personnel protection equipment corresponding with those findings utilized.

Level C - 0-5 ppm Gas/Vapor Concentration Above Background

Level C protection should be selected when the type(s) and concentration(s) of respirable material is known, has adequate warning properities, or is reasonably assumed to be not greater than the protection factors associated with air-purifying respirators; and exposure to the few unprotected areas of the body (i.e., neck) is unlikely to cause harm. Continuous monitoring of site and/or individuals must be established.

Level D

Level D is the basic work uniform and should not be worn as a form of protection in the Exclusion (contaminated) Area. Level D protection should only be selected when sites are positively identified as having no toxic hazard potential.

WORK ZONE DESIGNATIONS

An incident generally involves the escape of normally controlled substances into the environment via air, water, or land surface. Response activities involve actions to minimize and prevent these discharges. Site control is preventing or reducing the transfer of hazardous substances (contaminants) from the site by workers and equipment involved in site operations.

Site control involves two major activities: 1) physical arrangements and control of the site work areas; and 2) methods for the removal of contaminants from people and equipment.

Control is needed to reduce the possibility of transport of contaminants from the site which may be present on personnel and equipment. This can be accomplished in a number of ways including:

1. Physical barriers to exclude unnecessary personnel.
2. Checkpoints with limited access to the site or areas within the site.
3. Minimizing personnel and equipment on-site consistent with effective operations.
4. Establishment of containment zones.
5. Decontamination procedures.
6. Conducting operations in a manner to reduce possibility of contamination.

One method of reducing the potential for transfer of contamination is to delineate zones or work areas within the vicinity of the incident based upon expected or known levels of contamination. Within these zones, prescribed operations would occur utilizing appropriate personnel protective equipment. Movement between areas would be controlled at checkpoints. Three contiguous zones are recommended:

1. Exclusion Area (Contaminated)

The Exclusion Area is the innermost area and is considered contaminated or "hot". Within the Exclusion Area, prescribed levels of protection must be worn by all entering personnel. An entry check point must be established at the periphery of the Exclusion Area to control the flow of personnel and equipment between contiguous zones and to ascertain that the procedures established to enter and exit the zones are followed. The boundary should be physically secured, fenced, posted, or well defined by geographical boundaries.

The Exclusion Area is further subdivided into three (3) separate zones based on their known or potential levels of contamination. These zones are defined as follows and correspond to the associated Levels of Protection:

Zone A - The area of the greatest contamination potential; area requires highest level of respiratory, skin, and eye protection. This is a Level "A" personnel protection area (500 ppm to 1000 ppm).

Zone B - The area of next highest contamination potential; area requires highest level of respirator protection and lower level of skin and eye protection. This is a Level "B" personnel protection area (5 ppm to 500 ppm).

Zone C - The area where exposure potential, concentration, and/or route(s) at entry of contamination are relatively known and are assumed not greater than the protection factor associated with a full face mask air-purifying respirator. This is a Level "C" personnel protection area (Background to 5 ppm).

2. Support Area (Non-contaminated)

The Support Area is the outermost area of the site and is considered a non-contaminated or "clean" area. It is designated as a controlled traffic area for authorized support personnel and the location for support equipment (Command Post, Equipment Trailer, etc.). Potentially contaminated personnel clothing, equipment, etc., are not permitted.

3. Contamination Reduction Area

Between the Exclusion Area and the Support Area is the Contamination Reduction Area. The purpose of this zone is to provide an area to prevent or reduce the transfer of contaminants from the Exclusion Area. All decontamination activities occur in this area.

At the boundary between the Contamination Reduction Area and the Exclusion Area is the "Hot Line" and access control station. Entrance into the Exclusion Area requires the wearing of the prescribed personnel protection equipment which may be different than the equipment requirements for working in the Contamination Reduction Area.

Figure 1 illustrates Site Work Area Layouts while Figure 2 shows the organization and location of entry team members.

DECONTAMINATION

As a part of the system to prevent or reduce the physical transfer of contaminants by people or equipment from on-site to off-site areas, procedures must be instituted for decontaminating anything leaving the Exclusion Area and Contamination Reduction Area. These procedures include the decontamination and proper removal of protective equipment and also the correct method of removing personnel protective equipment to avoid transfer of contaminants from the clothing to the body. Unless otherwise demonstrated, everything leaving the Exclusion Area should be considered contaminated and appropriate methods established for decontamination or disposal. Consideration must also be given to the protection equipment worn by personnel operating the decontamination line.

Since it is virtually impossible to prevent the transfer of possible contaminants on protective clothing to the wearer, the mainline of defense is the thorough decontamination of the clothing. When done effectively, the amount of substance remaining on the suit is greatly reduced and the possibility of suit-to-wearer transfer is proportionately reduced.

Personnel equipment that has been worn into the Exclusion Area and subsequently decontaminated upon leaving the area, may need to be used in subsequent operations; therefore, it should be stored for air drying in the Support Zone.

In extreme situations, complete decontamination of personnel protective equipment, instruments, and small items may have to be done in a controlled laboratory situation.

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COMPRESSED BREATHING AIR PURITY

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The purity of compressed breathing air, as utilized in emergency crews' life support systems, takes on added significance not only because of the extremely hazardous nature of those professions falling within this classification, but also because of the temperature extremes in which these individuals operate. In the air processed by well maintained compressed breathing air systems, contaminants such as carbon monoxide, oxides of nitrogen and condensed hydrocarbons, are infrequently detected at concentrations that would be considered potentially hazardous to the end user. Water vapour however is often found in excessive amounts, and this constitutes the major reason for non-compliance with the purity requirements of CSA Standard Z180.1-M1978. This presentation will therefore deal mainly with those problems associated with excessive moisture in compressed breathing air, and will also touch on good practice procedures related to cylinder pressurizing and storage, particularly during cold weather operations.

With each passing year there is an ever increasing number of potentially toxic substances being released into the atmospheric environment, and very little is known of their short or long term impact on human health. It must therefore be assumed that air drawn from the lower atmosphere for the production of compressed breathing air, may contain harmful contaminants, and these must be removed to ensure that the processed end product is dry and of high purity. It is of vital importance then, that those individuals tasked with the responsibility of operating and maintaining breathing air compressors and associated system components, are highly competent. They must also be knowledgeable with respect to the mechanical filters and purification media essential for the removal of a wide range of particulates, airborne contaminants, compressor generated oil mists and water vapour.

All to frequently, salespersons representing manufacturers or distributors of breathing air purification systems provide the user with misleading and ambiguous instructions as to the care and maintenance of these units. It is absolutely meaningless to advise the purchaser that the purification package produces air that meets CSAZ180.1 standards, or that the unit has the capacity to process 100,000 cubic feet of air between each change of sorbent materials. Colour indicators designed to signal the end of cartridge service life leave the operator to decide the degree of colour change necessary before maintenance is required. To protect his investment, and ultimately the end user of the compressed air produced by these units, the prospective buyer should demand in writing, answers to such questions as: "What volume of air can be processed by the unit at an ambient dewpoint of e.g. -56.5°C (-70°F)?", or "Is the unit equipped with a catalyst for the conversion of carbon monoxide to the less harmful carbon dioxide, "and", at what point in the indicator colour change do the purification sorbents require replacement?"

The first question must also require that the air, apart from the specified dewpoint, must in all other respects meet the purity requirements of the CSA Z180.1-M1978 Standard. Upon completion of the processed air volume, a sample of the processed air should be collected, and analysed by a certified laboratory to determine whether or not the air conforms in all respects to the above purity standard.

The dewpoint of -56.5°C referred to in the second last paragraph is intended only as an example; the user must establish his dewpoint requirement based on the conditions and temperature extremes in which the compressed breathing air is to be used. Appendix C, a recent addition to CSA Z180.1-M1978 includes dewpoint correlation data for each of the four most common user system pressures. These tables will be discussed along with the maximum allowable limits for individually listed contaminants in Table 1 of CSA Z180.1.

Turning now to Table 1, (Table 2 of CSA Standard Z180.1-M1978), "Compressed Breathing Air", it can be seen that the first two components, carbon dioxide and carbon monoxide are set at maximum allowable concentrations of 500 mL/M^3 (ppm), and 5mL/M^3 (ppm), and represent levels equal to 1/10 of the Threshold Limit Value (TLV) as documented by the American Conference of Governmental Industrial Hygienists (ACGIH). The establishment of these limits were based primarily on two considerations:

(a) that compressed breathing air will also be used in diving and caisson work at increased partial pressures, and

(b) compressed breathing air is a processed product, and should therefore be at least as pure as the lower atmosphere from which it was obtained. Normal atmospheric air contains 200 to 400 parts per million of carbon dioxide; and the National Air Quality Objectives, as proposed by Environment Canada in 1976, are to maintain carbon monoxide levels at a maximum of 13 and 30 ppm for 8 hour and 1 hour exposures respectively.

Hydrocarbons in Table 1 have been separated into three groups, to allow the assignment of maximum allowable concentrations, these are:

(a) Total volatile non-substituted hydrocarbons as methane equivalents;

(b) Halogenated hydrocarbons, with specific compounds listed.

(c) Hydrocarbons (condensed or aerosol) and particulate matter.

Any other compounds not included under these groupings would be dealt with in accordance with the notes following Table 2 of the Standard.

Of all the samples analysed over an 18 year period of breathing air quality assurance, nitrogen dioxide has seldom appeared as a contaminant. Nitrous oxide on the other hand, is usually detected at levels between 0 to 0.3 ppm. This latter component has no assigned TLV, but 25 ppm frequently appears in the literature as a recommended ceiling limit.

The limit for condensed hydrocarbons (oil) was originally set in consideration of the possibity of high presence of polynuclear aromatic hydrocarbons (PAH) in commonly used compressor lube oils. A study performed under contract for DCIEM indicated that the PAH levels are in fact quite small. The 1 mg/M^3 limit is therfore considered adequate in terms of protecting the health of the user.

Water vapour, although not usually considered as a contaminant in compressed breathing air, can have harmful effects on components of the breathing air system, and can also lead to malfunctions in self contained breathing apparatus. It is therefore essential that compressed air systems operators have a working knowledge of dewpoints, and their relationship to breathing air safety. Dewpoint is defined as the temperature at which condensation of water vapour in air takes place. The measurement of dewpoint is usually carried out on air at normal temperature and pressure, i.e. at 20^{o}C and 101:3 kPa, but it may also be measured at line or cylinder pressure. It is the former measurement that frequently leads to confusion since a reported dewpoint of, for example, - 50°C is interpreted as the temperature at which the SCBA wearer can safely operate without having any fear of regulator freeze-up, or other moisture condensation problems. If we now look at the corresponding dewpoint at a service pressure of 2216 psig, it becomes evident that protection is afforded only to a temperature of -2°C. This relationship between the ambient and pressure dewpoints is shown in Tables 2 to 5 inclusive. For the example given above, refer to Table 3, where the dewpoint -51°C measured at normal temperature and pressure (column 1) has a water vapour content of 34 ppm by volume. When this same air is pressurized to 15.3 mPa (2216 psig), or 151 atmospheres, the pressure dewpoint shown in column 3 is -2°C, and the water vapour content is now 151 x 34 ppm or 5134 ppm. The worker using such air in subfreezing tmperatures would therefore be at risk due to equipment failure.

The four tables, providing ambient/pressure dewpoint correlations for sevice pressures of 689 kPa (100 psig), 15.3 mPa (2216 psig), 20.7 mPa (3000 psig) and 31 mPa (4500 psig), were recently added to the CSA Z180.1 standard as a reference for users in selecting the dewpoint appropriate to their requirement.

TABLE 2

Maximum Allowable Concentration of Contaminants

(By Volume, Measured at 21°C and 101.3 kPa)

Contaminant	Concentraton
Carbon dioxide	500 mL/m^3
Carbon monoxide	5 mL/m^3
Total volatile non-substituted hydrocarbons as methane equivalents	25 mL/m^3
Nitrogen dioxide	0.2 mL/m^3
Nitrous oxide	5 mL/m^3
Trichlorotrifluorethane*	2 mL/m^3
Dichlorodifluoromethane**	2 mL/m^3
Chlorofifluoromethane**	2 mL/m^3
Oil (condensed or aerosol) and inorganic particulate matter	1 mg/m^3
Water vapour ‡:	
(a) In air supplied at pressures above 1400 kPa	27 mL/m^3 (20 mg/m^3) - 53°C
(b) In breathing air delivered through pipelines:	

Dew-points, measured at line pressure for:

(i) **Outdoor installations** (where any part of the breathing air system is exposed to the outdoor atmosphere). The dew-point at line pressure shal be at least 10°C below the minimum local recorded ambient temperature at the plant site:

(ii) **Indoor installations** (where the entire breathing air system is installed indoors). The dew-point at line pressure shall be at least 10°C below the minimum temperature to which any part of the breathing air system is exposed at any season of the year. In no case should the dew-point at line pressure exceed 2°C.

Odour - Free from any detectable odour.
Others §

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* Commonly used as chemical cleaners.

** Commonly used as propellants and refrigerants. Their presence in the breathing air would be suggestive of inboard leaks in the system.

‡ Water in liquid or separated form shall be kept below the minimum to avoid growth of micro-organisms and malfunction of equipment.

§ Contaminants other than those listed in Table 2 shall not exceed the odour threshold, or 1/10 the Threshold Limit Value documented by the American Conference of Government Industrial Hygienists (ACGIH). The threshold limit value for total combined mixtures of contaminants as documented in current Threshold Limit Values (TLVs^R) for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes (Appendix C) of ACGIH shall apply. The values used in calculating mixtures shall be as in Table 2 or 1/10 of the current Threshold Limit Value as documented by ACGIH.

Table 2

Approximate Moisture Content in Compressed Breathing Air at 689.1 kPa (100 psig) Typical of a Low Pressure Breathing Gas Distribution System - Air Delivered Through Pipelines

Atmospheric Dewpoint Measured at 21°C & 101.3 kPa (14.7 psig)		Water Vapour Content At Atmospheric Pressure	Pressure Dewpoint At 689.1 kPa (100 PSIG 6.8 ATM)		Water Vapour Content at 689.1 kPa (100 PSIG)
Celsius°	Fahrehneit°	mL/M³ (ppm/v)	Celsius°	Fahrenheit°	mL/M³ (ppm/v)
-7	+19	3394	+20	+68	23,080
-8	+18	2996	+18	+64	20,370
-10	+14	2636	+16	+61	17,930
-13	+ 9	2035	+12	+54	13,840
-15.5	+ 4	1557	+ 8	+46	10,590
-18	0	1181	+ 4	+39	8,030
-22	- 8	885	0	+32	6,020
-25	-13	635	- 4	+25	4,320
-28	-18	450	- 8	+18	3,060
-32	-26	316	-12	+10	2,150
-35	-31	219	-16	+ 3	1,490
-38	-36	150	-20	- 4	1,020
-40	-40	124	-22	- 8	842
-42	-44	102	-24	-11	692
-44	-47	83	-26	-15	566
-46	-51	68	-28	-18	462
-47	-53	55	-30	-22	376
-49	-56	45	-32	-26	305
-50	-58	36	-34	-29	246
-52	-62	29	-36	-33	198

Table 3

Approximate Moisture Content in Compressed Breathing Air at 15.3 mPa (2216 psig) - Typical Pressure for Self-Contained Breathing Apparatus (SCBA)

Atmospheric Dewpoint Measured at 21°C & 101.3 kPa (14.7 psig)		Water Vapour Content At Atmospheric Pressure	Pressure Dewpoint at 15.3 mPa (2216 PSIG) 151 ATM		Water Vapour Content at 15.3 mPa (2216 PSIG)
Celsius°	Fahrenheit°	mL/M^3 (ppm/v)	Celsius°	Fahrenheit°	mL/M^3 (ppm/v)
-45.5	-50	68	+7	+45	10,268
-48.5	-55	48	+5	+37	7,248
-51	-60	34	-2	+28	5,134
-53	-63 (CSA)	27	-3	+24	4,077
-54	-65	24	-6	+21	3,624
-56.5	-70	17	-10	+14	2,567
-59.5	-75	11.5	-14	+ 7	1,737
-62	-80	8	-18	0	1,208
-65	-85	5.5	-22	- 8	831
-68	-90	3.5	-26	-15	529
-70.5	-95	2.3	-31	-21	347
-73	-100	1.5	-34	-29	227

Table 4

Approximate Moisture Content in Compressed Breathing Air at 20.7 mPa (3000 psig) - Typical Pressure for Divers Breathing Air

Atmospheric Dewpoint Measured at 21°C and 101.3 kPa (14.7 PSIG)		Water Vapour Content at Atmospheric Pressure	Pressure Dewpoint at 20.7 mPa (3000 PSIG) 204.1 ATM		Water Vapour Content at 20.7 mPa (3000 PSIG)
Celisius°	Fahrenheit°	mL/M^3 (ppm/v)	Celsius°	Fahrenheit°	mL/M^3 (ppm/v)
-45.5	-50	68	+12	+54	13,878
-48.5	-55	48	+ 7	+45	9,797
-51	-60	34	+ 2	+36	6,939
-53	-63 (CSA)	27	- 1	+30	5,510
-54	-65	24	- 2	+28	4,898
-56.5	-70	17	- 7	+20	3,470
-59.5	-75	11.5	-11	+12	2,347
-62	-80	8	-15	+ 5	1,663
-65	-85	5.5	-19	- 2	1,123
-68	-90	3.5	-24	-11	714
-70.5	-95	2.3	-28	-18	469
-73	-100	1.5	-32	-26	306

Table 5

Approximate Moisture Content in Compressed Breathing Air at 31.0 mPa (4500 psig) - High Pressure for Self-Contained Breathing Apparatus (SCBA)

Atmospheric Dewpoint Measured at 21°C & 101.3 kPa (14.7 PSIA)		Water Vapour Content at Atmospheric Pressure	Pressure Dewpoint at 31.0 mPa (4500 PSIG) 306 ATM		Water Vapour Content at 31.0 mPA (4500 PSIG)
Celsius°	Fahrenheit°	mL/M^3 (ppm/v)	Celsius°	Fahrenheit°	mL/M^3 (ppm/v)
-45.5	-50	68	+18	+64	20,808
-48.5	-55	48	+12	+54	14,688
-51	-60	34	+ 8	+46	10,404
-53	-63 (CSA)	27	+ 4	+39	8,262
-54	-65	24	+ 3	+37	7,344
-56.5	-70	17	- 2	+28	5,202
-59.5	-75	11.5	- 6	+21	3,519
-62	-80	8	-10	+14	2,448
-65	-85	5.5	-14	+ 7	1,683
-68	-90	3.5	-20	- 4	1,071
-70.5	-95	2.3	-24	-11	704
-73	-100	1.5	-28	-18	459

There is however, one further factor to be considered in determining a safe dewpoint, and this being adiabatic expansion of the air from cylinder to SCBA regulator pressure. In 3000 psig SCBA cylinder, air expansion from cylinder to regulator pressure during heavy user demand, may cause the air to cool by as much as 5°C. The user can now establish the required dewpoint by utilizing the dewpoint tables 2-5, as follows:

(a) Select the Table appropriate to the pressure of the user system;

(b) Determine the averge ambient temperature of the use-environment;

(c) Locate this temperature in the third column headed pressure dewpoint;

(d) Select the nearest temperature 5°C below this to allow for adiabatic cooling of the air;

(e) The temperature directly opposite this in the first column (atmospheric dewpoint) is the required dewpoint.

It would be prudent to strive for low dewpoint air throughout the year, as a means of preventing equipment malfunction in cold weather, and internal corrosion in storage, and pressurized SCBA cylinders.

Two examples of dewpoint selection to meet specific ambient temperature requirements, are given as follows:

Example #1: The diver, using a 20.7 mPa (3000 psig) air supply is engaged in winter diving, in which the water temperature is at the freezing point, i.e., 0°C (32°F).

(a) Select Table C3 (20.7 mPa/3000 psig)

(b) The ambient water temperature is 0°C

(c) Locate 0°C in Column 3 headed pressure dewpoint (-1°C is the closest listed temperature)

(d) Select a temperature 5°C below this temperature, still in column 3. (The closest temperature is -7°C)

(e) The temperature directly opposite this in column 1 "Atmospheric Dewpoint" is -56.5°C (-70°F), and corresponds to a water vapour content of 17 ppm/v

The required atmospheric dewpoint for winter diving is therefore -56.5°C (-70°F).

Example #2: A firefighter using a 15.3 mPa (2216 psig) air supply is operating in a geographical location where the average winter temperature is -26°C (-15°F)

(a) Select Table 2 (15.3 mPa/2216 psig)

(b) Average ambient temperature -26°C

(c) Locate -26°C in column 3 "Pressure Dewpoint"

(d) Select temperature 5°C below this 31°C/-21°F

(e) The dewpoint opposite in column 1 under the heading "Atmospheric Dewpoint" is -70.5°C/-95°F, and correspoinds to a water vapour content of 2.3 ppm/v

The required dewpoint for air used by the firefighter is therefore -70.5°C/-95°F.

To ensure that the compressed breathing air being produced is of high quality, and in compliance with the air purity standard, samples should be forwarded to a laboratory, certified to perform such analyses at least twice each year. The samples should be submitted in gas sample transit units designed and approved for this purpose, to ensure that the sample is truly representative of the system. Clean dry respirable air submitted in other everyday cylinders may become contaminated due to residual material in the cylinders from previous use.

Included in the care and maintenance of cylinders for SCBA, are such items as filling, storage, periodic inspection, rotation in use and hydrostatic testing.

Filling

The filling of cylinders from a storage reservoir or a cascade, system should be carried out at a rate not exceeding an averge of 300 psig per minute. Rapid or schock charging is a dangerous practice, and could result in a serious equipment malfunction. First of all, rapid compression of air causes a large heat increase, not only of the air within the cylinder, but more importantly in the cylinder valve itself. This excessive heat can damage the frangible disc or fusible plug, causing it to leak or otherwise malfunction. Secondly, when rapidly filled cylinders cool, they are well below service pressure and require topping up. Immersion of the cylinder in a water bath has absolutely no value in cooling the cylinder, because in the short time required for filling, even at the prescribed rate of 300 psig per minute, the cooling effect of the water would not penetrate the cylinder wall to influence the compressed air temperature. Also, there is the danger of overfilling the water bath and allowing water to enter the valve.

Storage

Cylinders should, whenever possible, be stored in a warm, dry place, and in a vertical valve up attitude. This provides some measure of protection for those cylinders that have been filled with compressed air having a high water vapour content. Water vapour condensation due to compression, and cooling in cold weather will tend to accumulate in the cylinder over a period of time. Horizontal storage of such cylinders increases the water-metal interface, and produces conditions favouring line pitting corrosion, reportedly the most serious type, and possible oxygen reduction, particularly in steel cylinders that have been stored but unused over a period of several months. Oxidation in aluminum cylinders is admittedly less extensive on the internal cylinder walls, but in the presence of an electroyte, galling and corrosion may occur in the valve threads. This is so because many aluminum cylinders have brass valves, some of which are chromium or cadmium plated. This affords a great deal of protection, but only if the dip tube is also plated to reduce the dissimilar metal condition. As a precaution, steel cylinders, pressurized but not used over a 3-month period, should be slowly depressurized and refilled with clean dry air. Extensive studies carried out by the University of Rhode Island, Ocean Engineering Department, have clearly demonstrated that pressurized cylinders containing moisture can undergo serious corrosion damage in as little as 3 months storage. The most serious cases involved steel cylinders containing salt water, and revealed extensive pitting corrosion and reduction in wall thickness by as much as two thirds. Other cases have been reported in the literature where corrosion in steel SCBA cylinders has depleted the oxygen content to below life support levels in as little as 3 months. Aluminum cylinders in the study suffered some damage, but this was far less extensive.

Inspection

All cylinders, whether of steel or aluminum construction, should be inspected internally at least once a year. This can best be accomplished through planned maintenance by withdrawing a block of cylinders from service each month. After careful removal of the valve, the internal surfaces should be inspected for the presence of moisture and/or condensed hydrocarbon (oil), and also any evidence of pitting or scaling. Steel cylinders requiring extensive cleaning may be sand or shot blasted, but such abrasive cleaning should be ridigly avoided in aluminum cylinders. Aluminum cylinders showing heavy deposits or laminar scaling should be dealt with in accordance with manufacturer's instructions. It is strongly recommended that maintenance personnel refer to Compressed Gas Association (CGA) Pamphlets C6 and C6.1 for detailed guidance on inspection of cylinders.

Cylinder Use Rotation

Cylinders in current use should be numbered, coded or stored in a manner that ensures that all are used on a regular rotation basis. This is an important step in preventing the use of the same cylinders time after time; while others remain idle, and may require depressurizing and refilling after the 3 month non-use period. When surplus cylinders are withdrawn from service and placed in long term storage, they should be reduced in pressure to approximately 40-50 psig, and stored vertically, valve up. The reduced partial pressure of oxygen and water vapour in the cylinders will reduce the possibility of corrosion damage. The above ambient pressure also ensures that the valve remains closed and this prevents the entry of dust, moisture and airborne contaminants.

Hydrostatic Testing

The hydrodstatic testing frequency for compressed air cylinders varies from 3 years for the hoop wrapped and fully composite fibreglass/resin wrapped cylinders, to 5 years for steel and unsupported seamless aluminum cylinders. The larger 220 and 300 cubic foot cylinders used in cascade and storage reservoirs require retesting every 10 years. In recent years there have been reports of cylinders that were reported to have successfully passed the hydrotest, but were found to be so extensively corroded, that the ability to even pass a visual inspection was indeed questionable. In the United States, some agencies performing this service were exposed as frauds, having only a hammer and stamp as equipment. Such extreme criminal malpractices, it is hoped are few and far between, but they do unfortunately cause doubt and concern in the minds of those requiring this necessary service to be performed with confidence. The user is therefore urged to demand of the testing agency such information as the method used and the standard that is referenced in his performance of the service. He should also insist that the agent provide a written report detailing his findings, and also a data sheet showing the volumes measured during each phase of the test. Any testing agency that is unable to provide the correct information regarding the first two questions, should in itself justify seeking the service elsewhere.

The author has been intrinsically involved both with the development and implementation of breathing gas quality assurance programs since 1965, first as a member of the Department of National Defence at the Defence and Civil Institute of Environmental Medicine (DCIEM), and currently at Mann Testing Laboratories in Rexdale, Ontario.

This paper and its contents are based almost exclusively on personal experiences in the analysis of breathing-life-support-gases for a wide range of users including Canadian Hospitals, Industry, Fire Service, The Department of National Defence, Sport and Commercial Diving. A great deal of work has also been performed in support of the Attorneys General in the investigation of fatal accidents in which self-contained breathing apparatus was used.

The greatest benefits derived from this service have been through educational feedback to individual users in the field, and through dissermination of information to larger groups in the industry at large, via conferences and workshops.

SOME OPERATING PROBLEMS ASSOCIATED WITH PERSONAL PROTECTION EQUIPMENT AT SPILL INCIDENTS

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Hazardous materials emergency response teams face numerous unknowns when responding to a spill incident. Considerable effort has gone into classifying, labelling and placarding hazardous matrials for transportation in order to assist people involved in the transportation or clean-up of these materials.

The selection of the personal protection equipment that may be used by the hazardous materials emergency response team appears to have been influenced by:

(a) equipment currently in use by the organization sponsoring the haz-mat team
(b) personal opinion
(c) lack of understanding of how certain classes and types of equipment work and if really sutiable for use by haz-mat teams.
(d) reluctance to examine new, non-traditional approaches to handling emergencies.

Consequently, during and following a chemical spill incident, it is not unusual to hear complaints such as:

- couldn't see, lens fogged,
- not enough air or none on inhalation,
- air mask service time too short,
- facepiece leaked,
- frozen regulator,
- poor communication,
- too cumbersome,
- too heavy,
- suit too hot or too cold,
- suit too clumsy,

and many more too numerous to mention.

Personal protection equipment is usually designed to provide protection for the:

- head
- eyes and face
- hearing
- feet
- skin
- hands and fingers
- respiratory system

Equipment is also available to provide protection against heat, cold, slips and falls.

This discussion will deal with two prime areas:

- respiratory protection
- skin protection (total body).

Operating problems associated with personal protection equipment can be reduced or eliminated by some or all of the following:

- match equipment to the hazard,
- ensure integrity and compatibility of the equipment,
- wearer's visibility and orientation remains near normal,
- pre-determine actual practical working time and update as work progresses,
- consider worker fatigue and discomfort,
- programmed maintenance and inspection,
- sustained training program.

Self-contained breating apparatus (SCBA) is first-line equipment for any haz-mat team and is probably the least understood. Most of the SCBA used by haz-mat teams is of the pressure demand type wherein a positive pressure is maintained in the facepiece during inhalation and is less apt to permit inward leakage of contaminants.

Most people accept that pressure demand SCBA is at least 200 times safer than demand SCBA, yet in many cases, the use of pressure demand SCBA has resulted in reduced service time.

Some people even stated they could still smell smoke and gases even though they were using pressure demand SCBA. Inward leakage has occurred!

- Why could this happen?
- What was the cause?
- What could be done to correct it?

Inward leakage on a pressure demand facepiece is not normal. However, it can and does happen when the prssure in the facepiece drops below atmospheric pressure during the inhalation phase and accompanied by a poor facepiece seal. Should this happen in a toxic or hazardous atmosphere, the SCBA wearer could be at risk.

Pressure demand SCBA may go negative if one or more of the following conditions exist:

- regulator is out of tune and cannot supply the user's demand;
- regulator design is such that it cannot supply the user's demand;
- cylinder valve is not fully open;
- mainline valve is not fully open;
- combination of both of the above;
- regulator freezes or operates in a sluggish manner because the air in the cylinder does not have a pressure dewpoint suitable for the ambient temperature (low temperature operation).

Unless there is a leak in the face to facepiece seal, the service time between a demand and pressure demand SCBA should be identical.

Outward facepiece leakage to atmosphere with accompanying reduction of service time can be caused by:

- improper size of facepiee for the wearer,
- facial hair,
- facial shape,
- protective equipment interfering with the seal,
- cut or torn sealing surface,
- improper storage ... deformed facepiece.

Some other causes of reduced service time are:
- loose connections in the air supply system, particularly from the regulator to the facepiece;
- cylinders not charged to their full rated working pressure;
- cylinders filled too fast to the rated working pressure, thereby generating heat. When cooled to ambient temperatures, the pressure is lowered and service time is reduced.

To resolve some of these operating problems, new equipment with longer rated service time is not always the answer.

The tendency to change to SCBA with longer rated service time will result in burdening the wearer with SCBA (34.7 lbs.) that is larger and marginally below the upper weight limit of 35 lbs. set by NIOSH.

Dramatic breakthroughs were achieved during the 1970's. The weight of most SCBA was reduced from the 30 to 32 pound range to a range of 24 to 25 pounds by the use of new technology in manufacturing cylinders for compressed air. Stress on the wearer was reduced and effectiveness increased.

Investigation has revealed that persons using a 30 to 32 pound SCBA could expect to have their work efficiency reduced by approximately 20 percent. Consider the potential for reduced efficiency and effectiveness when a person wears SCBA that is near the NIOSH upper weight limit of 35 pounds.

This is not to say that there is no need for long service SCBA. Special applications will no doubt require this type of equipment. However, be aware of the limitations and demands imposed by this type of equipment on the wearer and on the administration of haz-mat teams.

Well-trained people using properly selected equipment that has been well maintained will probably resolve most of the operating problems associated with SCBA, especially if CSA standard Z94.4-M1982, "Selection, Care and Use of Respirators," is used as the basis for the program.

An option to obtaining longer service time without reverting to heavier, bulkier, high pressure (4500 PSIG) SCBA is to consider the use of dual-purpose SCBA. These are in the lightweight range, using readily available compressed air at 2216 PSIG and by the use of airline hose in lengths up to 300 feet per SCBA, provide virtually an unlimited supply of breathing air from a remote source.

In addition to increased time at the work site, this approach reduces or may eliminate the necessity of contaminated workers having to return to the fresh air base to be fitted with a new cylinder of compressed breathing air.

Depending upon the type and class of contaminant, it may not be feasible to change air cylinders without risking contamination of the support crew, their equipment and possibly the wearer. Consequently, it is possible that SCBA may be used once and have to be taken out of service for complete decontamination. Serious logistic problems may result in the supply of sufficient SCBA and spare compressed air cylinders to complete the job.

Depending upon the type and class of contaminant, maintaining the integrity of the fresh air base may be at risk each time contaminated people return for cylinders of fresh air.

If danger of fire, over-exposure to radiation or injury from moving structures or wreckage is minimal, then it appears that the most efficient approach would be to use dual-purpose SCBA with a remote air supply.

Should an injury occur to a worker in a contaminated area, a rescue team can move in with a portable air cylinder and quickly connect to his airline connection on the dual-purpose SCBA and prepare the worker properly for movement to a safe area minimizing the possibility of aggravating the injury. This action would not likely be the case should the worker be using a standard 30 or 60-minute pressure demand SCBA.

Depending on the nature of the injury and whether removal of wreckage was required, the danger of the injured person running out of air is real. As this point nears, does the rescue team:

- risk moving the victim without proper preparation to avoid aggravation of the injury?
- if the victim is trapped, do they risk breaking the integrity of his life support system to change cylinders or apply a facepiece from another SCBA?
- leave because their own air supply is near the end-point?

Consider the many options available with a duel-purpose pressure demand SCBA in any of the above situations.

Use of total body encapsulating life support systems complete with respiratory protection equipment is now common and long overdue. Part of this life support system is a total body covering that integrates with suitable SCBA. For the purpose of this discussion, the total body covering will be called a chemical suit.

Chemical suits have been available for many years, but have gained prominence only in the last five or six years.

Generally, they are supplied in two modes:

(A) Totally encapsulates the body including the entire SCBA.

(B) Totally encapsulates the body, however, the SCBA is worn externally.

Opinions differ widely as to which mode should be used. When the potential use of this class of protective equipment is not fully explored, haz-mat teams may end up with suits and SCBA that do not integrate properly and may present a hazard to the user greater than the contaminant in question.

In order to place the selection of a chemical into perspective, please consider these two approaches:

SCBA INSIDE OF SUIT

ADVANTAGES	DISADVANTAGES
1. SCBA IS PROTECTED AGAINST EFFECTS OF THE CONTAMINANTS.	1. WEARER DOES NOT HAVE READY ACCESS TO THE CONTROLS OF THE SCBA, NAMELY THE BY-PASS OR PURGE VALVE.
2. NIOSH CERTIFICATION OF THE SCBA IS MAINTAINED.	2. WEARER MUST LEARN TO USE NEW PROCEDURES TO REACH THE BY-PASS OR PURGE VALVE BY REMOVING HIS HAND FROM THE GLOVE - A DIFFUCULT CHORE.

SCBA INSIDE OF SUIT (CONTINUED)

ADVANTAGES	DISADVANTAGES
	3. WEARER DOES NOT KNOW HIS AIR PRESSURE
	4. WEARER MUST TAKE THE FOLLOWING PRECAUTIONS: A) HE MUST USE ONLY FULL TANKS. B) HE CAN WITHDRAW HIS HAND FROM THE GLOVE AND RETRACT HIS ARM FROM THE SLEEVE INTO THE SUIT AND OPEN THE BY-PASS OR PURGE VALVE. C) TIME REQUIRED TO ACCOMPLISH ACTION (B) WHEN CLOTHED FOR COLD WEATHER OR LOW TEMPERATURE OPERATONS (HEAVY UNDERWEAR, SWEATERS OR PARKAS WORN INSIDE THE SUIT). HOW DOES ONE TRAIN WEARER NOT TO PANIC AND HOLD HIS BREATH DURING THE TIME IT TAKES TO RESTORE THE AIR FLOW? D) IF A "BUDDY" IS PRESENT AND SIMILARLY DRESSED, HOW MUCH HELP CAN THE WEARER'S "BUDDY" EXTEND UNDER THESE CONDITIONS? E) IT IS HIGHLY LIKELY THE WEARER OR THE "BUDDY" WOULD BREAK THE INTEGRITY OF THE SUIT (OPEN ZIPPER OR CUT THE FABRIC) TO OPEN THE BY-PASS OR PURGE VALVE TO RESTORE THE AIR FLOW.
	5. CAN WEARER HELP HIMSELF USING THE ARM RETRACTION PROCEDURE IF HE IS INJURED OR TRAPPED? A) IF THE WEARER IS INJURED AND MUST BE MOVED TO A FRESH AIR BASE, THE INTEGRITY OF THE SUIT AND SCBA MUST BE MAINTAINED. HOW IS THIS ACCOMPLISHED WHEN WEARING A 30 OR 60-MINUTE SCBA? SUBTRACT THE TIME OF ENTRY, EXIT TIME, TIME FOR DIAGNOSING TYPE OF INJURY AND OBTAINING ADDITIONAL HELP OF A STRETCHER TEAM OUTFITTED SIMILARLY TO THE NOW INJURED PERSON, PREPARING HIM FOR MOVEMENT, PLACING HIM IN STRETCHER AND ACTUAL REMOVAL TO FRESH AIR BASE.

SCBA INSIDE OF SUIT (CONTINUED)

ADVANTAGES	DISADVANTAGES
	PICTURE THREE SCENARIOS:
	- RAILWAY EMBANKMENT, WRECKED RAIL CARS, WINTER, SNOW, DARKNESS, TOXIC OR CORROSIVE ATMOSPHERES.
	- CHEMICAL PROCESS AREA, WORKING ONE OR TWO LEVELS ABOVE GROUND, ONLY ACCESS IS A CAGED LADDER, TOXIC OR CORROSIVE ATMOSPHERE.
	- CONFINED SPACE WITH ALL THE RAMIFICATIONS.
	B) MOVING AN INJURED PERSON SAFELY WITHOUT AGGRAVATING THE INJURY WHILE HE IS WEARING AN SCBA INSIDE A TOTAL ENCAPSULATING SUIT BEFORE HIS AIR SUPPLY IS EXHAUSTED, IS A CHALLENGE THAT MAY NOT BE SUCCESSFULLY OVERCOME.
	6. NORMAL VIEWING (BY THE WEARER) OF THE SCBA GAUGES IS IMPOSSIBLE.

SCBA INSIDE OF SUIT (CONTINUED)

ADVANTAGES	DISADVANTAGES
	7. MOIST, EXHALED AIR FROM FACEPIECE MAY FOG LENS OF CHEMICAL SUIT.
	8. VISION MAY BE DISTORTED BECAUSE THE WEARER HAS TO LOOK THROUGH THE LENS OF THE SCBA AND THE LENS OF THE CHEMICAL SUIT.
	9. FIELD OF VISION IS REDUCED (WHEN NEEDED MOST).
	10. EFFECTIVE WORKING TIME IN A TOXIC OR CORROSIVE ATMOSPHERE WILL BE REDUCED BECAUSE WEARER MUST RETURN TO FRESH AIR BASE TO EXCHANGE AIR CYLINDERS FOR FULL ONES.
	11. EFFICIENCY AND SAFETY OF THE OPERATION AND PERSONNEL IS COMPROMISED.
	12. EACH TRIP TO REPLACE AIR CYLINDERS ON SCBA INSIDE THE CHEMICAL SUIT RESULTS IN THE FOLLOWING:

SCBA INSIDE OF SUIT (CONTINUED)

ADVANTAGES	DISADVANTAGES
	A) POTENTIAL CONTAMINATION OR INJURY OF SUPPORT TEAM.
	B) SUPPORT TEAM MUST BE OUTFITTED SIMILARLY TO THE WORKING TEAM IN ORDER TO DECONTAMINATE THE WEARERS' SUITS PRIOR TO OPENING THEM TO REPLACE THE AIR CYLINDERS (THE PROPER DECONTAMINATING AGENT MAY NOT BE AVAILABLE).
	C) POTENTIAL CONTAMINATION OF THE SAFE, FRESH AIR BASE, RENDERING IT UNSAFE FOR SUBSEQUENT USE AND REQUIRING THE CREATION OF A NEW FRESH AIR BASE.
	D) A LOGISTICS PROBLEM QUICKLY DEVELOPS UNDER THE AFOREMENTIONED CONDITIONS.
	13. USE OF DUAL-PURPOSE SCBA IS VIRTUALLY IMPOSSIBLE. CONSIDER THE FOLLOWING:
	A) THE QUICK DISCONNECT FITTING ON THE REMOTE AIRLINE (AN ADAPTER HOSE AND FITTING REQUIRED TO

SCBA INSIDE OF SUIT (CONTINUED)

ADVANTAGES	DISADVANTAGES
	PENETRATE THE WALL OF THE SUIT) WOULD BE VIRTUALLY IMPOSSIBLE TO "BREAK" SO THAT AIR FROM THE CYLINDER ON THE SCBA WOULD FLOW AUTOMATICALLY TO THE WEARER ON INHALATION.
	B) EVEN THOUGH THE QUICK DISCONNECT FITTING WERE ENLARGED SO THAT THE WEARER COULD OPERATE IT THROUGH THE WALL OF THE SUIT, THE WEARER WOULD BE WITHOUT AIR FOR THE TIME IT TOOK TO ACCOMPLISH THIS ACTION.
	C) SOME DUAL-PURPOSE SCBA REQUIRE THE CYLINDER VALVE (ON WEARER'S BACK) TO BE CLOSED WHEN USING AIR FROM A REMOTE SOURCE, THEN OPENED MANUALLY SHOULD THE REMOTE AIR SUPPLY BE INTERRUPTED. ACCOMPLISHING THIS BY ATTEMPTING TO LOCATE AND OPEN THE VALVE ON THE SCBA CYLINDER WORN INSIDE THE SUIT MAY PROVE TO BE SOMEWHAT DIFFICULT.

SCBA INSIDE OF SUIT (CONTINUED)

ADVANTAGES	DISADVANTAGES
	D) THE WEARERS OF CHEMICAL SUITS WOULD LIKELY BE WEARING COVER GLOVES OVER THE BUTYL RUBBER GLOVES (WHICH HAVE LOW CUT AND ABRASION RESISTANCE) AND COVERED WITH A CONTAMINANT THAT MAY BE GREASY AND SLIPPERY. ACCOMPLISHING THE ACTION IN #13 A), B), AND C) IS HIGHLY UNLIKELY.
	14. WHEN THE WEARER REALIZES THAT HE CANNOT GET ANY AIR UNTIL HE "BREAKS" THE QUICK DISCONNECT OR OPENS THE CYLINDER VALVE, HE WILL RESORT TO HIS BY-PASS OR PURGE VALVE AND ENCOUNTER ALL OR MOST OF THE ASSOCIATED PROBLEMS INDICATED IN POINTS #1 TO #5.
	15. DIFFICULT TO USE THE SCBA AND CHEMICAL SUIT WITH THE STANDARD PROTECTIVE FIREFIGHTING TURN-OUT COATS, PANTS, BOOTS, HELMETS, ETC.

SCBA INSIDE OF SUIT (CONTINUED)

ADVANTAGES	DISADVANTAGES
	16. NECESSITATES USING SCBA IN A NON-APPROVED MANNER.
	17. GOOD, CLEAR COMMUNICATION BY RADIO OR TELEPHONE IS SERIOUSLY IMPEDED.
	18. CONSIDER A HAZ-MAT TEAM HANDLING AN EMERGENCY THAT IS CORROSIVE, RADIOACTIVE, OR INVOLVING HIGHLY TOXIC BACTERIA. COULD CYLINDER CHANGES BE MADE OR NEW SCBA DONNED WITHOUT RISK OF CONTAMINATING THE WEARER OR THE INSIDE OF HIS SUIT IF IT ENCAPSULATES THE SCBA? DECONTAMINATE HIM FIRST? WILL THE RIGHT DECONTAMINATION AGENT BE AVAILABLE ON SITE?

SCBA OUTSIDE OF SUIT

ADVANTAGES	DISADVANTAGES
1. THE WEARER HAS QUICK READY ACCESS TO ALL THE CONTROLS OF THE SCBA, INCLUDING THE BY-PASS OR PURGE VALVE.	1. SCBA IS EXPOSED TO TOXIC, CORROSIVE ATMOSHPERES AND MAY REQUIRE REPLACEMENT OF SOME PARTS.
2. THE WEARER CAN USE THE STANDARD OPERATING INSTRUCTIONS (AS FURNISHED BY MANUFACTURER) IN OPERATING THE SCBA. THERE IS NO NECESSITY TO LEARN A SEPARATE PROCEDURE FOR THE SCBA WHEN USED WITH A CHEMICAL PROTECTION SUIT.	2. APPARENTLY, THE NIOSH CERTIFICATION FOR THE SCBA MAY BE VOID, DEPENDING UPON THE METHOD OF ATTACHING THE SCBA FACEPIECE TO THE CHEMICAL SUIT.
3. THE SUIT IS LIGHTWEIGHT AND LESS BULKY AND EASIER TO WEAR WHEN "BAT WINGS" ARE NOT INCORPORATED AS PART OF THE SUIT.	3. IF POINT #2 IS A FACT, THEN THE OWNER OF THE SUIT MAY HAVE TO APPLY FOR A VARIANCE TO THE REGULATORY AUTHORITY HAVING JURISDICTION.
4. IF THE WEARER'S AIR SUPPLY IS INTERRUPTED, HE HAS FAST, READY ACCESS TO THE BY-PASS OR PURGE VALVE WITHOUT THE POSSIBILITY OF:	

SCBA OUTSIDE OF SUIT (CONTINUED)

ADVANTAGES	DISADVANTAGES
A) EMOTIONAL UPSET, BORDERING ON PANIC. B) HAVING TO REMEMBER SPECIAL TRAINING ON HOW TO REACH THE BY-PASS OR PURGE VALVE. C) BEING ENCUMBERED BY HEAVY CLOTHING USED TO PROTECT AGAINST LOW TEMPERATURES. D) BEING FORCED TO GO WITHOUT AIR FOR A PERIOD LONGER THAN THAT WHICH A PERSON COULD HOLD THEIR BREATH WHILE ATTEMPTING TO ACTIVATE THE BY-PASS OR PURGE VALVE. E) PANIC.	
5. THE WEARER'S "BUDDY" HAS FULL ACCESS TO THE CONTROLS OF THE WEARER'S SCBA IN THE EVENT THE WEARER HAS ANY DIFFICULTY IN THEIR OPERATION.	

SCBA OUTSIDE OF SUIT (CONTINUED)

ADVANTAGES	DISADVANTAGES
6. THERE IS NO NECESSITY TO BREAK THE INTEGRITY OF THE SUIT BY OPENING THE ZIPPER OR CUTTING INTO THE SUIT TO REACH THE CONTROLS OF THE SCBA.	
7. BY USING ONLY DUAL-PURPOSE SCBA WITH REMOTE AIR SUPPLY, VIRTUALLY AN UNLIMITED SERVICE TIME IS AVAILABLE WITH THE FOLLOWING BENEFITS: A) INJURED PEOPLE CAN HAVE THEIR INJURIES PROPERLY DIAGNOSED, BE PREPARED PROPERLY FOR MOVEMENT REDUCING THE POSSIBILITY OF FURTHER AGGRAVATING THEIR INJURIES. B) IF THEY ARE TRAPPED OR CANNOT BE MOVED READILY TO FRESH AIR, THEY HAVE ACCESS TO AN UNLIMITED SUPPLY OF BREATHING AIR FROM REMOTE LOCATIONS UP TO 300 FEET.	

SCBA OUTSIDE OF SUIT (CONTINUED)

ADVANTAGES	DISADVANTAGES
8. THE WEARER CAN EASILY VIEW THE AIR PRESSURE GAUGE.	
9. LENS FOGGING IS VIRTUALLY ELIMINATED WHEN A PROPERLY FITTED NOSECUP IS USED WITH THE FACEPIECE.	
10. VISION IS CLEAR AND UNDISTORTED THROUGH THE FACEPIECE LENS.	
11. NORMAL FIELD OF VISION IS MAINTAINED.	
12. WORKING TIME IN A TOXIC OR CORROSIVE ATMOSPHERE CAN BE EXTENDED FOR SEVERAL HOURS BY USING THE DUAL-PURPOSE SCBA WITH UP TO 300 FEET OF AIRLINE HOSE ATTACHED TO A REMOTE SUPPLY OF COMPRESSED BREATHING AIR.	

SCBA OUTSIDE OF SUIT (CONTINUED)

ADVANTAGES	DISADVANTAGES
13. THE FOREGOING APPROACH TO HANDLING AIRBORNE CONTAMINANTS IS SAFER AND MORE EFFICIENT BECAUSE: A) NO NECESSITY FOR THE WEARER TO RETURN TO FRESH AIR EVERY 30 OR 60 MINUTES TO REPLACE THE SPENT CYLINDER. B) LOWER FREQUENCY OF EXPOSURE OF THE SUPPORT TEAM TO THE CONTAMINATED PERSON AND HIS EQUIPMENT HELPS MAINTAIN THEIR INTEGRITY. C) REDUCED POTENTIAL FOR POSSIBLE CONTAMINATION OF THE FRESH AIR BASE.	
14. STANDARD PROTECTIVE FIREFIGHTING COATS, PANTS, BOOTS, HELMETS, ETC. CAN BE USED WHEN NECESSARY.	

SCBA OUTSIDE OF SUIT (CONTINUED)

ADVANTAGES	DISADVANTAGES
15. GOOD, CLEAR COMMUNICATION BY RADIO, TELEPHONE OR PERSON-TO-PERSON IS POSSIBLE BY USING THE SPEAKING DIAPHRAGM IN THE NORMAL MANNER.	
16. THE SCBA CAN BE USED SAFELY IN THE NIOSH APPROVED MANNER.	

DECONTAMINATION OF THE CHEMICAL SUITS, REGARDLESS OF WHETHER THE SCBA IS WORN INSIDE OR OUTSIDE, MAY NOT ALWAYS BE FEASIBLE.

- WILL SUFFICIENT DECONTAMINATION AGENT BE READILY AVAILABLE?
- IF WATER IS THE DECONTAMINATING AGENT, WHAT ARE THE DISPOSAL PROBLEMS?
- WHAT IS THE DECONTAMINATION PROCEDURE IF THE CONTAMINANT ON THE SUIT IS A WATER-REACTIVE CHEMICAL?
- HOW IS DISPOSAL OF THE RESIDUE HANDLED?
- WHAT IF CONTAMINANT IS BACTERIOLOGICAL OR RADIOACTIVE?

CHANGING COMPRESSED AIR CYLINDERS EVERY 30 OR 60 MINUTES COULD BECOME A MAJOR PROBLEM. CONSIDER THE MANY OPTIONS AFFORDED BY A DUAL-PURPOSE PRESSURE DEMAND SCBA WHEN WORN ON THE OUTSIDE OF TOTAL BODY ENCAPSULATING LIFE SUPPORT SYSTEMS.

Operating problems associated with personal protection equipment at spill incidents can be minimized or eliminated by operating the haz-mat program on a sustaining basis in accordance with CSA Standard Z94.4-M1982, "Slection, Care and Use of Respirators".

The following are mandatory for a successful program:

- Define the program
- Definitions - terminology
- Develop respiratory protection program
- Program administration ... assigned accountability
- Hazard identification
- Selection of appropriate respirator
- Respirator facial fit
- Training
- Use of respirators
- Cleaning, maintenance and storage or respirators
- Health surveillance of respirator wearers
- Program evaluation

A final word about training. To be effective, training with SCBA and chemical suits should include scheduled exercises that will stress the wearer over the full rated service-time of the SCBA.

Training sessions should be conducted in all types of weather, temperature and wind conditions and on all types of terrain, including deep snow. Detailed records on the type of training and service-time achieved with the SCBA should be maintained for every member of the haz-mat team.

Personal protection equipment, properly selected and maintained for proper use by well-trained and supervised haz-mat teams, can be expected to meet performance requirements with a minimum of operational problems.

U.S. EPA, ERT'S INITIAL AIR MONITORING GUIDES FOR CHEMICAL SPILLS

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INTRODUCTION

The U.S. Environmental Protection Agency's Environmental Response Team (ERT) was established in October 1978 to provide technical assistance to On-Scene Coordinator's (OSC), Regional Response Team (RRT), National Response Team (NRT), EPA Headquarters, and Regional Offices, as well as other Government Agenices in the area of emergency environmental issues, such as chemical spills and uncontrolled hazardous waste sites.

This paper describes the air monitoring guides used by ERT for the initial monitoring/classification of ambient/workplace air conditions during an accidental chemical release (e.g., warehouse fire, train derailment, transportation accident.) It describes the objectives of using total atmospheric gas/vapor concentrations; on-site/off-site analysis of organic gases/vapors; sampling; collection media; and specific contaminant identification.

The following are only a few of the many factors involved in developing a site specific air monitoring program: equipment availability, collection media(s), flow rates(s), analytical protocol, analysis time, detection limit, wind speed, ambient temperature, atmospheric conditions, operational cost, etc. In addition to these factors, where do you start your monitoring and what logical approach do you follow?

OBJECTIVES

A number of air hazards may be present during a spill response:

- ° Combustible gases that can lead to fires and explosives
- ° Oxygen deficiencies
- ° Radiation
- ° Toxic organic and inorganic gases or vapors

Procedures for assessing the first three are relatively straightforward and are documented in occupational safety and health literature. If the types of gases/vapors are known, they can be measured with properly calibrated instruments or standard industrial hygiene procedures. When little is known of the contaminants present or concentrations of individual constituents, the analysis problem is more difficult.

The objectives are simply to obtain reasonable balance between cost, personnel requirements, accuracy, detection limits, analytical turnaround time, and laboratory availability. Our approach achieves a reasonable balance between these factors by the use of direct reading instruments (DRI) and off-site laboratory analysis by an accredited American Industrial Hygiene Association laboratory.

Two types of field instruments, flame ionization detector (FID) and photoinoization detector (PID), are capable of detecting most volatile organic compounds associated with an environmental emergency. They may be used to make the initial site survey and/or to collect continuous air monitoring data during response operations.

Since the field FID and PID are small portable instruments, they cannot be expected to yield results as accurate as laboratory instruments. However, they are relatively easy to use when detecting total organic concentrations of known contaminants in air, but the interpretation of data becomes more difficult when trying to identify the components of a mixture.

The following is a list of equipment used to perform all phases of the ERT five (5) step air monitoring guides:-

- Portable Photoionization Detector (PID)
- Portable Organic Vapor Analyzer (GC/FID)
- Low Flow Personnel Sampling Pumps (e.g. 10 cc/min. to 100 cc/min.)
- High Flow Personnel Sampling Pumps (e.g. 200 cc/min. to 3-l/min.)
- Tenax Thermal Desorption Collection Tubes (metal)
- Carbon Sphere Thermal Desorption Collector Tubes (metal)
- Carbon Filled Glass Sampling Tubes (150 mg and 600 mg)
- Particulate Cassettes
- Cool Packs
- Thermal Storage Containers

FIELD PROCEDURES

In general, the FID and PID instruments may be used for four of the following five steps at a particular response.

Each of the steps for detecting gas/vapor contaminants is built on the previous step and helps to further characterize the concentrations measured by the two instruments. The fifth step, particulate sampling, is totally independent of the previous four steps and is based primarily on knowledge of the incident.

Step I - Determine Background Concentrations

To establish background levels of air pollution in the vicinity of a chemical spill, the initial step is to collect samples in upwind areas not suspected to contain contaminants. It is important to avoid locations such as freeways, active industrial sites, etc., that are readily accessible but may not give a true picture of prevailing conditions in clean areas nearby. Depending on the situation, monitoring may be done in the area adjacent to the incident to determine if contaminants are leaving the area.

In addition to setting up air pumps with appropriate collection media in the background area, FID/PID direct reading instrument readings should be taken.

Step II - Determine Concentrations On-Site

The initial on-site survey is conducted with FID/PID direct reading instruments (DRI's) to determine general site ambient conditions, and/or to locate the "so-called" hot spots. In addition, data obtained with DRI's during the survey should be compared with the backround data.

The total gas/vapor concentrations should be measured near any suspected contaminated area (both ground level and breathing zone), being careful to avoid transient contaminants such as heavy equipment.

If possible another survey should be made at the background station and a rough sketch made of the site.

Step III - On-Site Area Samples

On-site air monitoring may vary from two to four times daily depending on several factors such as as wind speed/direction and temperature. The number of sampling stations and locations, as well as sampling train, vary with atmospheric conditions. In addition to a control (background) station, there should be stations within the suspected contaminated area(s) and downwind near the site boundary. Stations should be set up where total gas/vapor concentrations are the highest or suspected.

Stations consist of personnel monitoring pumps with appropriate collection media. The type of pumps, media, and flow rates will vary per incident. For example, personnel sampling pumps with a flow rate of approximately 100 cc/min., thermal desorption tubes (e.g. carbon spheres/Tenax) and an Organic Vapor Analyzer with a programmable thermal desorber are commonly used. The sampling pumps are run at about 100 cc/min for sufficient time to collect 15-30 liters. Samples are desorbed and analyzed on-site with a field FID to determine the number of peaks and total concentrations.

Initially, morning and afternoon samples should be collected to establish a baseline both on-site and background. Total gas/vapor concentrations should be measured at the start and finish of each sample collection. A suggested format for reporting/calculating total gas/vapor concentrations is shown in in Table No. 1.

Step IV - Identify Specific Contaminants (if needed)

When specific information is needed on the contaminants, additional personnel monitoring pumps should be run, this time with both thermal desorption tubes (e.g. Tenax/carbon spheres) and carbon filled glass tubes. Generally, when the total gas/vapor reading and the number of peaks obtained in Step III are low, a 150 mg carbon filled glass sampling tube should be used and operated long enough at a flow rate of 100 cc/min. to pull 15 to 30 liters of air, depending on suspected contaminants and their concentrations.

When total gas/vapor reading and the number of peaks identified in Step III are high, a 600 mg carbon filled glass sampling tube should be operated long enough at a flow rate of 1/2-2 liters/minute to pull 90 to 150 liters of air, depending on the suspected contaminants and their concentrations.

If desorption equipment is not available for routine monitoring, 100 mg carbon filled glass sampling tubes should be collected routinely and analyzed off-site until sufficient background data has been collected. Off-site analysis should be conducted, as close as possible, following the National Institute of Occupational Safety and Health (NIOSH) P&CAM Analytical Method No. 127 by an accredited American Industrial Hygiene Association laboratory. Table II lists the organic solvent identified with this metnod. Samples should be held by the laboratory for possible gas chromatography/mass spectrometry analysis until the On-Scene Coordinator releases them.

If other than organic solvents are suspected, then the NIOSH Manual of Analytical Methods (Vol. 1-7) should be consulted for the appropriate collection media and flow rates.

If the recently developed ERT 2-stage tube field tests are successful, then the numbers of 150 mg/600 mg carbon tubes as well as other widely used media may be reduced. This tube was developed on state-of-the-art technology with the objective of developing convenient screening media for air samples at sites where unknown/multiple contaminants may be present. Since this tube has only been used three times in the field at the writing of this paper, a conclusion can not be drawn at this time.

Step V - Identify Particulate Contaminants (if needed)

Samples for particulates may be collected at any time. Since the collection media vary tremendously, the NIOSH Manual of Analytical Methods (Vol. 1-7), should be consulted for those methods routinely used in industry. The use of portable real-time aerosol monitors may be extremely helpful in trying to select the sampling station location.

CONCLUSION

Although this paper describes the initial ERT Air Monitoring Program, it does not address an entire occupational and/or public health air monitoring program. The use of this program in conjunction with a complete occupational health and safety program, has proven to be extremely useful.

Acknowledgment

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TABLE No. 1

1. Volume sampled by "MDA Accuhaler 808" Personal Sampling Pump:
   Volume sampled (cc's) = final stroke count - initial stroke count

   X cc's/stroke*

   X Multiplier factor for orifice used**

   *Specified on pump itself.
   **Specified in operations manual and Table 1.

   Sample Calculation:

   At beginning of sampling period, Accuhaler stroke counter reads 16292.9. At the end of sampling period, it reads 16632.9. What is the volume of air sampled?

   Volume sampled (cc) = 16632.9 - 16292.9

   X 5.7 (cc/pump stroke)

   X 1.1 (multiplier for orifice)

   Volume Sampled = 2131.8 cc or 2.1 liters.

2. Reporting Format

   a. Total GC Mode: Time Weighted Average (Using OVA Thermal Desorber)

   $$\text{TWA (ppm)} = \frac{\text{Volume desorbed (liters)} \times \text{concentration (ppm)}}{\text{Volume collected (liters)}}$$

   $$= \frac{0.300\ \text{(liters)} \times 22\ \text{(ppm)}}{2.1\ \text{(liters)}}$$

   $$= 3.14\ \text{ppm as } CH_4 \text{ (methane)}$$

   b. Peaks: GC mode

   ° 4 peaks observed (none measured)

   ° attached chromatograph

TABLE II

Organic Solvents Identified by P&CAM Analytical Method No. 127

Organic Solvent	Molecular Weight
Acetone	58.1
Benzene	78.1
Carbon tetrachloride	154.0
Chloroform	119.0
Dichloromethane	84.9
p-Dioxane	88.1
Ethylene dichloride	99.0
Methyl ethyl ketone	72.1
Styrene	104.0
Tetrachloroethylene	166.0
1,1,2-trichloroethane	133.0
1,1,1-trichloroethane (methyl chloroform)	133.0
Trichloroethylene	131.0
Toluene	92.1
Xylene	106.0

Reference: NIOSH Manual of Analytical Methods
U.S. Department of Health Education & Welfare
Public Health Service Center for Disease Control
National Institute of Occupational Safety & Health
DHEW (NIOSH) Publication No. 77-157-A.

PERSON-PORTABLE SYSTEMS FOR MULTI-MEDIA ANALYSIS AT CHEMICAL SPILL SITES

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INTRODUCTION

The mandate of Environment Canada's Environmental Emergencies Technology Division (EETD) includes responsibility for developing and coordinating federal programs aimed at achieving technologically sound and effective response capabilities for spills of environmentally hazardous substances. Originally formed in 1972 as the Environmental Emergencies Branch (EEB), EETD research and development activities have, until recent years, focused primarily on the oil spill problem, particularly with respect to the arctic marine environment. While federal initiatives in this area continue, a comprehensive program to develop chemical spills response capabilities was launched in 1980 and is known as the Chemical Hazard Emergency Countermeasures (CHEC) Program.

Many hazardous chemical spill incidents involve a single substance which is easily identifiable from evidence at the scene or from shipping documents. While the substance and perhaps even the spill volume may be known, rapid implementation of the correct response measures (which may include evacuation of the area, shutting down water treatment plants, etc.) requires 1) a knowledge of the chemical, physical, toxicological and environmental properties of the substance involved, and 2) rapid and sufficiently accurate determination of air, water, and soil concentrations of the chemical in the vicinity of the spill site. A well known example illustrating the need for preparedness in these areas is the Macgregor derailment incident of 1980 (1). Several days passed before reliable measurements of vinyl chloride concentration levels in air were obtained.

The authors have been contracted since June, 1983 to continue development on two levels of the analytical component of the CHEC program. This paper is intended to serve as a summary of 1) the concepts upon which the analytical program is based, 2) the current development status of EETD person-portable analytical systems for spill site use, and 3) our projection of future development possibilities at this level of analytical sophistication.

ANALYTICAL PROGRAM CONCEPTS

General Concepts

One of the first tasks in the development program was an assessment of existing analytical capability in terms of potential applicability to spill monitoring. Based on criteria of portability, accuracy, and complexity, existing capability was divided into five levels, as shown in Table 1. Levels 1, 2 and 3 were considered most appropriate for spill monitoring. This paper focuses on the development of Level 2.

TABLE 1
EETD DESIGNATION OF ANALYTICAL LEVELS

Level	Description	Portability	Coverage	Status
1	Small detector system (usually colourimetric, e.g., Drager tubes)	Pocket-portable	Approx. 100 substances	Several commercially available units
2	Electronic detector systems (meters)	Person-portable	Perhaps 1000 substances	Development required
3	Computer-controlled instruments with pre-developed software	Vehicle portable (small van)	Perhaps 10,000 substances	Development required
4	Mobile laboratories	Towable on good roads	As many as preparations are made for	Several prototypes exist, not very useful for rapid spill work in remote areas
5	Fixed laboratories	Not portable	As above	Existing and not very useful for spill work

Level 2 Concepts

Level 2 analytical systems are person-portable field units intended for use directly at a spill site. The relative lack of sophistication associated with Level 2 systems actually enhances their potential for spill site use. Although many Level 2 systems for air monitoring are non-specific with respect to substances detected, this does not represent a serious drawback since, in many spill situations, only one hazardous substance is involved, and concentration levels of this substance are likely to far exceed levels of potential interferences in the ambient background. The electronic detection, direct readout requirement for Level 2 systems minimizes operator subjectivity in interpreting results. Important criteria to be met by Level 2 systems include:

a) rapidity in obtaining results
b) accuracy
c) ability to provide detection limits below maximum allowable limits for a wide range of hazardous substances of interest
d) simplicity of use and maintenance
e) adaptable for use over a wide range of climatic conditions
f) long-life self-contained power source
g) moderate cost to allow for wide distribution across Canada.

Given the frequency of spill incidents, the varying degrees of immediate human and environmental impact represented by such incidents, and the high probability that a specific spill location is remote from the location of Level 3 systems, it is obvious that the typical spill situation must be handled by Level 1 and Level 2 analytical systems standing alone. Also, since these systems are likely to be operated frequently by field personnel with little background in chemistry, it is important to understand and minimize the effect of design and performance, chemical, environmental, and human factors which contribute to error. Accuracy of results with Level 2 systems will depend on the following:

a) accuracy of calibration or standardization
b) inherent stability of instrument response
c) proper maintenance of equipment
d) chemical interferences
e) reagent shelf-life
f) ambient environmental conditions at the spill site
g) training of field personnel, following thorough laboratory evaluation of systems
h) quality of Field Manuals.

We see Level 2 systems as being applicable to air, water and soil analysis. In terms of rapidity and accuracy of data, the order of media priority is the same as above. Air is generally the medium associated with the greatest immediate potential hazard in spill situations. Soil/sediment analysis is seen as being useful for defining spill perimeters and monitoring the progress of cleanup operations such as excavation or dredging.

Priority Substances List

In order to focus the development of analytical capability on appropriate targets, a priority list of 150 chemical substances or groups was developed by the EETD (2). This priority list is specifically tailored to the current spill situation in Canada.

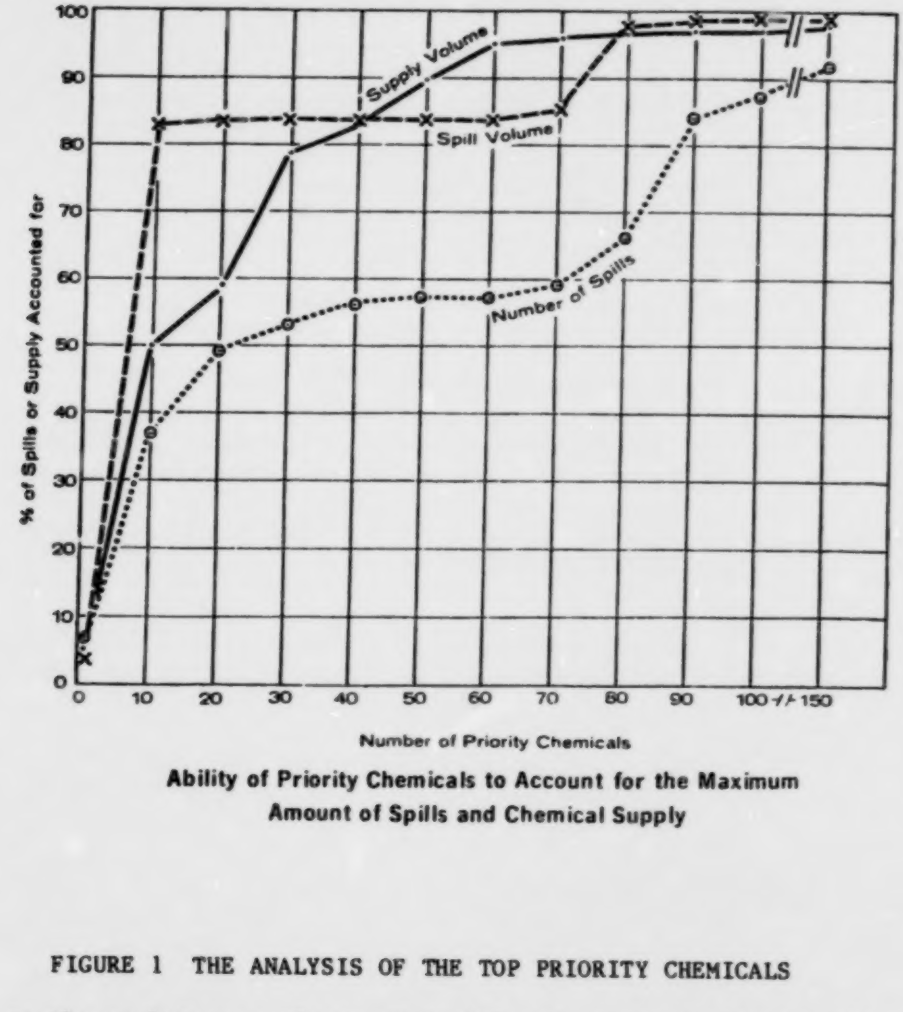
Figure 1 illustrates the correlation between number of spills, spill volume, and supply volume (production plus importation) for the 150 priority chemicals. Certain substances of high chronic toxicity and widespread environmental concern, such as PCBs, have been included in the list despite low rankings in terms of supply and spill volume. Since a higher percentage of small volume spills of such substances tend to be reported to environmental authorities relative to lower-profile chemicals, a sharp rise is observed in the spill number curve between 80 and 90 on the horizontal axis.

As seen from Figure 1, the first ten chemicals alone amount for 37% of the number of spills, 50% of the supply volume and 83% of the spill volume. By extending the number of chemicals to 150 we account for over 90% of the reported spills and well over 90% of the spill volume.

EETD LEVEL 2 ANALYTICAL CAPABILITY

Review of Existing Level 2 Analytical Systems

Having developed Level 2 concepts and criteria as well as the priority chemicals list, the EETD proceeded to assess the potential application of commercially available analytical instrumentation to spill site use. It was clear from this assessment that, for various reasons, very few instruments



Ability of Priority Chemicals to Account for the Maximum Amount of Spills and Chemical Supply

FIGURE 1 THE ANALYSIS OF THE TOP PRIORITY CHEMICALS

currently on the market were of any potential use to the Chemical Spill Monitoring Program. It was also clear that those systems which did show Level 2 potential would require extensive laboratory development work before being field-ready.

Table 2 lists the 150 EETD priority chemicals along with specific chemical/medium situations which the authors consider at this time to be both environmentally significant and potentially amenable to analysis by Level 2 systems. Certain situations were easily excluded from consideration. For example, air monitoring capability for a great many inorganic chemicals does not warrant consideration. Inorganic gases which are likely to evolve from priority substances in spill situations include ammonia, chlorine, hydrogen sulfide, sulfur dioxide, nitrogen oxides and hydrogen cyanide. All except the latter two substances are themselves present on the priority list. In many cases, however, the decision as to whether a particular situation was or was not significant and potentially amenable to Level 2 analysis was a subjective judgement based on many factors. These factors included vapour pressure, complexity and/or variability of chemical composition or formulation, reactivity in a medium, and chronic and acute toxicity properties. This data, as well as a great deal of other information specifically relevant to chemical spill response work, is contained in the draft version of an EETD manual being developed concurrently with the analytical program (3).

TABLE 2
EXISTING AND PROJECTED LEVEL 2 ANALYTICAL CAPABILITY FOR EETD PRIORITY HAZARDOUS SUBSTANCES IN AIR, WATER AND SOIL

THE 50 HIGHEST PRIORITY CHEMICALS (In alphabetical order)	A	W	S		A	W	S
Acetic Acid	1	1	2	Naphtha	1	-	-
Acetic Anhydride	1	1	2	Natural Gas (CH_4)	C1	-	-
Ammonia	1	1	2	Nitric Acid	X	1	2
Ammonium Nitrate	-	1	2	Phenol	1	1	2
Ammonium Phosphates	-	1	2	Phosphoric Acid	X	1	2
Benzene	C1	2	3	Phosphorus	-	1	2
Butyraldehydes	1	2	3	Potash (KCl)	-	1	2
Calcium Chloride	-	1	2	Propylene Oxide	1	3	-
Calcium Oxide/Hydroxide	-	1	2	Propylene	1	3	-
Carbon Dioxide	X	1	-	Sodium Chlorate	-	1	2
Chlorine	CX2	1	2	Sodium Chloride	-	1	2
Cyclohexane	1	3	3	Sodium Hydroxide	-	1	2
Ethylbenzene	1	2	3	Sodium Hypochlorite	-	1	2
Ethylene Dichloride	1	3	3	Sodium Sulfate	-	1	2
Ethylene Glycol	1	2	2	Styrene (Monomer)	1	2	3
Ethylene Oxide	C1	3	-	Sulfur Dioxide	CX2	1	-
Ethylene	1	3	-	Sulfuric Acid	X	1	2
Ferric Chloride	-	1	2	Sulfur	-	2	3
Formaldehyde	C1	2	2	Tetraethyl Lead	1	2	3
Hydrogen Chloride/Acid	X2	1	2	Toluene	1	2	3
Hydrogen Fluoride/Acid	X2	1	2	Urea	-	2	3
Hydrogen Sulfide	C1	1	2	Vinyl Chloride	C1	2	3
Mercury	CX	1	2	Xylenes	1	2	3
Methanol	1	2	2	Zinc Sulfate	-	1	2
Morpholine	1	2	2	2-Ethylhexanol	1	2	3

TABLE 2 (Continued)
EXISTING AND PROJECTED LEVEL 2 ANALYTICAL CAPABILITY FOR EETD
PRIORITY HAZARDOUS SUBSTANCES IN AIR, WATER AND SOIL (CONT'D)

THE SECOND GROUP OF PRIORITY CHEMICALS (100 substances or groups)

	A	W	S		A	W	S
Acetone	1	2	2	Hydrazine	X2	2	2
Acetylene	1	-	-	Hydrogen	X	-	-
Acrylonitrile	1	2	3	Hydrogen Peroxide	X	2	-
Adipic Acid	-	2	2	Isopropanol	1	2	3
Aluminum Chloride	-	1	2	Isopropylbenzene	1	2	3
Aluminum Hydroxide	-	1	2	Latex	-	3	3
Aluminum Sulfate	-	1	2	Lead Chromate	-	1	2
Aminocarb Pesticide	-	-	-	Lead Oxides	-	1	2
Ammonium Chloride	-	1	2	Magnesium Hydroxide	-	1	2
Ammonium Sulfate	-	1	2	Malathion	-	-	-
Arsine	X2	2	2	Maleic Anhydride	-	2	3
Barium Sulfate	-	1	2	MCPA	-	-	-
Benzoic Acid	-	2	3	Methyl Ethyl Ketone	1	2	3
Borax	-	1	2	Methyl Isobutyl Ketone	1	2	3
Boric Acid	-	1	2	Methyl Methacrylate	1	3	3
Butanols	1	2	3	Methylamines	1	2	3
Butylene	1	3	-	Methylene Chloride	1	3	3
Calcium Carbide	-	1	2	Nitrilotriacetic Acid	-	2	3
Calcium Carbonate	-	1	2	Nitroglycerine	-	-	-
Calcium Hypochlorite	-	1	2	Nonyl Phenol	-	2	3
Calcium Phosphate	-	1	2	n-Hexane	1	3	3
Caprolactam	-	2	3	PCBs	-	-	-
Carbaryl	-	-	-	Pentachlorophenol	-	2	3
Carbofuran Pesticides	-	-	-	Pentaerythritol	-	2	3
Carbon Disulfide	1	2	3	Perchloroethylene	1	3	3
Carbon Tetrachloride	1	3	3	Phthalic Anhydride	-	2	3
Chlordane	-	-	-	Potassium Hydroxide	-	1	2
Chloroform	1	3	3	Potassium Sulfate	-	1	2
Copper Sulfate	-	1	2	Propylene Glycols	1	2	2
Cresols	1	2	3	Sodium Aluminate	-	1	2
Dicamba	-	-	-	Sodium Arsenite	-	2	2
Dichlorobenzene	1	2	3	Sodium Borohydride	-	1	2
Dimethyl Ether	1	2	-	Sodium Carbonate	-	1	2
Dimethyl Terephthalate	-	3	3	Sodium Cyanide	X2	1	2
Dinoseb	-	-	-	Sodium Dichloroisocyanurate	-	1	2
Diphenylmethane-4,4'-	X2	-	-	Sodium Dichromate	-	1	2
Diisocyanate (MDI)				Sodium Hydrosulfite	-	1	2
Ethanol	1	2	2	(Dithionite)			
Ethanolamine	1	2	2	Sodium Phosphates	-	1	2
Ethylene Dibromide	1	3	3	Sodium Silicates	-	1	3
Fenitrothion	-	-	-	Sodium Sulfite	-	1	2
Fluorochloromethanes	1	3	-	Sulfuryl Chloride	X2	1	2
Formic Acid	1	1	2	Tall Oil	-	-	-

TABLE 2 (Continued)
EXISTING AND PROJECTED LEVEL 2 ANALYTICAL CAPABILITY FOR EETD PRIORITY HAZARDOUS SUBSTANCES IN AIR, WATER AND SOIL

	A	W	S		A	W	S
Terephthalic Acid	-	2	3	Yellow Cake	-	-	-
Terphenyls	-	3	3	Zinc Chloride	-	1	2
Titanium Dioxide	-	2	3	Zinc Oxide	-	1	3
Triallate Pesticides	-	-	-	1,1,1-Trichloroethane	1	3	3
Trichlorfon Pesticides	-	-	-	1,3-Butadiene	1	3	-
Trifluralin Pesticides	-	-	-	2,4-D (2,4-Dichlorophenoxyacetic Acid)	-	-	-
Trinitrotoluene	-	-	-	2,4-Toluene Diisocyanate	X2	-	-
Turpentine	1	3	3				
Vinyl Acetate	1	2	3				
TOTAL					73	126	115

C = Commercially available, factory-calibrated for substance.
X = EETD Level 2 systems do not possess analytical capability for substance in air.
- = Situations considered non-applicable to Level 2 analysis.
1,2,3 = Method development by April, 1984/1985/1986 respectively.
• = Require capability for hydrogen cyanide in air.

Having cautioned that many entries in Table 2 are, of necessity, partly subjective in origin and subject to re-evaluation, the number of applicable situations for air, water, and soil are 73, 126, and 115 respectively.

Dealing with water first, the few commercially available systems which are compatible to some degree with Level 2 criteria are similar in that coverage is basically restricted to inorganic species, and for a given species the same well-established colourimetric, titrimetric, or turbidimetric methodology is employed by all systems.

Available systems differ, however, in range of coverage for priority chemicals and general sophistication. A projection of April, 1984 as the completion date for analytical development of applicable water situations in Table 2 indicates that the Level 2 water analysis system selected by the EETD already possesses analytical capability for those specific chemicals.

For priority chemicals in spill site soil, a suitable analytical system is not commercially available. However, if we accept a lower accuracy, many of the existing Level 2 water analysis methods also will apply to soil analysis if the soil sample is first extracted with water. Progress in the area of soil analysis capability awaits the development of simplified extraction procedures and apparatus. For this reason, plus the generally lower priority associated with the soil medium in spill situations, completion dates for method development in this area is not projected before April, 1985.

A large number of instruments designed for air monitoring applications and satisfying some Level 2 criteria are on the market (4). The major shortcoming of many of these instruments in terms of the priority chemicals list is range of coverage. Many instruments are capable of measuring only a small number of specific chemicals in air, the most common examples being SO_2, H_2S, Cl_2, and NO_x. A few instruments are calibrated for one substance but have broad potential application. A small sub-group of these instruments satisfy the majority of the Level 2 criteria.

In Table 2 it is seen that a Level 2 air monitoring capability requirement is indicated for 73 chemicals or groups. If one wanted to buy an instrument or instruments which would accurately measure, off-the-shelf, any or all of these 73 chemicals, one would be buying 9 separate units for 9 chemicals, which represents 12% of the applicable air monitoring situations. Chemicals for which factory calibrated person-portable units are available are indicated by a C in the air column of Table 2. Obviously, instruments with potential for broad range coverage must be employed for the air monitoring component of the analytical program. Also, instruments must be calibrated for each chemical to which their detectors respond if reliable spill site data is to be obtained.

While some important gaps exist in the range of coverage associated with the present EETD Level 2 air monitoring systems, we expect to have fully developed analytical capability for 56 chemicals (77% of applicable situations) by April, 1984. In section 4 of this paper we will return to the scheduling aspect of the Level 2 development work.

The Level 2 analytical systems selected by the EETD for the Chemical Spill Program were the Foxboro Model 128 Organic Vapor Analyzer (OVA) plus the HNU Systems Inc. Model PI101 Photoionization Analyzer for air monitoring, and the HACH DR-EL/4 system for water and soil analysis. These systems are shown in Figures 2, 3 and 4 respectively. A brief description and discussion of each system follows.

OVA 128

The OVA 128 is basically a portable flame ionization detector designed for one-man, one-hand operation and weighing approximately 5 Kg. This type of detector exhibits inherently high sensitivity and responds to a very broad range of organic chemicals. In operation, a continuous metered flow of sample air is drawn into the detector chamber where organic molecules are burned in a hydrogen flame, producing positively-charged carbon-containing ions. These ions are driven to a negatively charged collector electrode where a current is generated which is proportional to the ion collection rate. This current is measured with a pre-amplifier, the output signal from which is further amplified and displayed as a parts per million reading on the meter assembly situated on the hand-held probe assembly.

In the "sniffer-mode" described above, the detector responds to all organic chemicals in the sample air. As discussed earlier, for spill monitoring work this lack of specificity will not seriously affect the accuracy of the results. The OVA 128 may also be operated in the Gas Chromatography (GC) mode if more than one organic compound is present in the air sample at concentration levels which would seriously affect accuracy of results for the pollutant of interest when the OVA is operated in the sniffer mode.

The OVA's hydrogen supply and rechargeable 12V DC battery allow for a minimum of 8 hours of continuous operation. A strip chart recorder is available as an option.

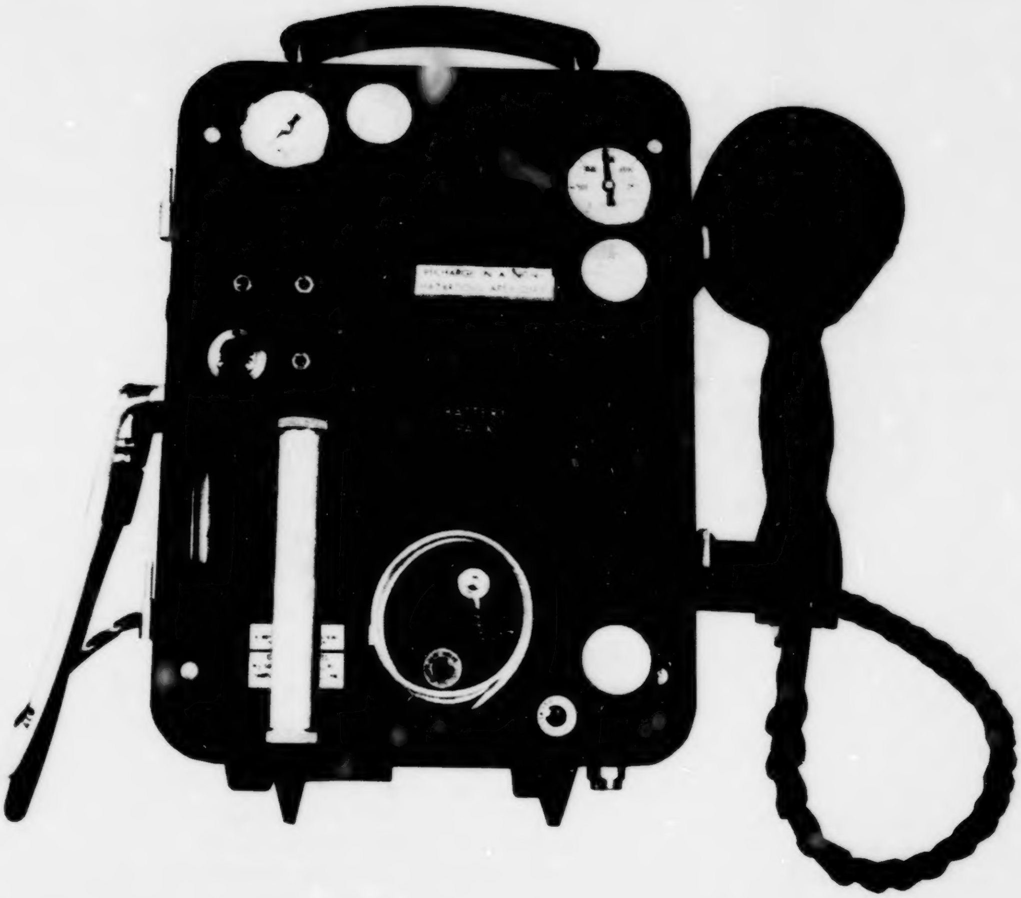


FIGURE 2 OVA 128

The OVA is calibrated for methane and has a useful concentration range for this compound of 0.1 to 1000 ppm. The linear and useful ranges for other priority organic chemicals will vary, and must be determined empirically. The OVA is capable of monitoring concentration levels below the TLV for the great majority of organic chemicals on the EETD priority chemicals list.

HNU PI-101

The HNU is an elegant and simply-designed detector unit which weighs approximately 4 Kg and consumes no gases. Detection of chemicals in air is based on the photo-ionization principle. During operation, a continuous flow of sample air is drawn by a DC-operated fan into an ionization chamber located in the hand-held probe. Photons emitted by the 10.2 eV UV source pass through a transmitting window into the ionization chamber where this radiation is

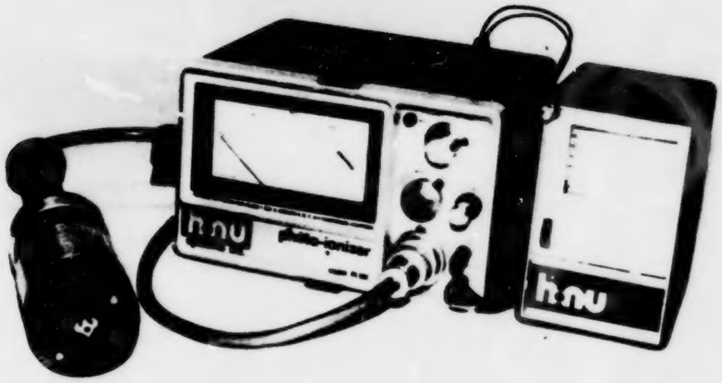


FIGURE 3 HNU PI-101

absorbed by molecules having ionization potentials of 10.2 eV or less (although substances with slightly higher ionization potentials typically produce an instrument response also). This process results in the formation of ions according to the equation:

$$RH + hv \rightarrow RH^+ + e^-$$

where RH is the sample molecule and hv is a 10.2 eV photon. The positive ions produced by this reaction are driven to a collector electrode, where a current proportional to the concentration of the sample substance in air is generated. This current is amplified and used to drive an analog meter on the readout unit.

The HNU is a selective detector, since chemicals having ionization potentials much greater than 10.2 eV will not be ionized and therefore will not produce an instrument response. For example, the HNU will not respond to major constituents of air such as O_2, N_2, CO, CO_2 and H_2O. The HNU, is however, capable of detecting a broad range of organic compounds, as well as a few inorganic compounds such as H_2S and NO_2.

Similar to the OVA, the HNU utilizes a rechargeable battery which allows for 10 hours of continuous service, or 5 hours of continuous service if the optional strip chart recorder is used.

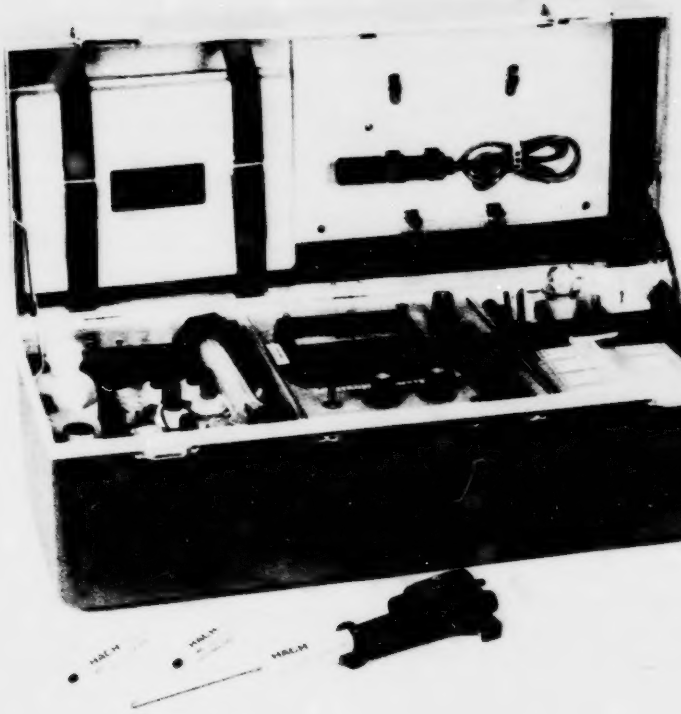


FIGURE 4 HACH DR-EL/4

The HNU is factory-calibrated for benzene and has a useful range of 0.1 to 2000 ppm for this chemical. The useful linear range for many chemicals is reported to be 0.1 to 600 ppm, although, like the OVA, the HNU must be calibrated for each priority chemical of interest to which it will respond. The HNU is capable of detecting concentration levels well below existing NIOSH, OSHA, and ACGIH limits for most priority chemicals to which it will respond.

Due to their dissimilar detection principles and their broad overlap in range of coverage, the OVA and HNU are complementary systems. This is a very desirable feature, especially for spill site air monitoring applications, since it allows for cross-checking of results. While close agreement between concentration readings from the two systems is not confirmation of accuracy, widely dissimilar results are a sure indication that equipment malfunction, operator error, or inaccurate calibration has occurred in at least one case.

HACH DR-EL/4

The HACH DR-EL/4 is considered to be the most analytically sophisticated Level 2 system for water analysis on the market and provides a broader coverage for EETD priority inorganic chemicals compared to competitive systems.

The HACH kit encompasses a large number of water quality tests normally performed on a routine basis at municipal and industrial water treatment facilities. HACH methods are generally based upon well established colourimetric, titrimetric, and turbidimetric reactions. After purchasing the basic kit consisting of a single-beam, portable spectrophotometer (conductivity feature optional), digital pH meter, digital titrator (micro-buret) and common labware, one need only purchase those chemicals and pre-standardized reagents required for the test factors of interest. A large number of dry reagents are available in single-dose form, conveniently sealed inside polyethylene "powder pillows" which are opened with ordinary nail clippers. Calibrated meter scales are provided for all test factors which require spectrophotometric analysis.

HACH technology minimizes the skill and technique factor typical of wet-chemical analyses to the point where water quality tests can be reliably performed by non-technical personnel. This feature, combined with the direct read-out capability and portability of the kit makes the HACH DR-EL/4 an attractive Level 2 system for spill response applications. There remains, however, a great deal of scope for development of the HACH kit, as described in the following section.

WORK IN PROGRESS AND FUTURE DEVELOPMENT

In order to have confidence that OVA and HNU instruments are operating properly, it is first necessary to have a practical appreciation of the inherent limits of performance variability associated with each instrument. Our first task must therefore be to conduct a performance evaluation of the OVA and HNU systems. The performance characteristics to be evaluated include: 1) accuracy of manufacturer's calibration, 2) linearity of response, 3) response time, 4) zero drift, 5) span drift (short-term calibration stability) and 6) long-term calibration stability.

Following the performance evaluation, the OVA and HNU will be calibrated for the EETD priority chemicals to which they respond, over concentration ranges appropriate for each substance. The calibration program will be based on the use of static test atmospheres of the chemicals of interest contained in fluorocarbon sampling bags at ambient pressure. To determine actual rather than nominal concentrations of priority chemicals in test atmospheres, and to monitor possible changes in concentration over the course of the calibration experiments, each calibration mixture will be sampled and analyzed by gas chromatography at frequent intervals. Assuming satisfactory instrument performance over the duration of a calibration experiment, a transparent meter-scale overlay based on the calibration data will be prepared for the OVA or HNU.

Each priority chemical for which an entry of 1 appears in the air column of Table 2 is considered to be amenable to analysis by the OVA, HNU, or in most cases, both systems.

The entries in Table 2 indicate that the OVA and HNU do not possess the required monitoring capability for 17 priority chemicals, including chlorine, hydrogen cyanide and sulfur dioxide, to pick three important examples. Level 1 (detector tubes) capability is available for all but perhaps two of these substances. Also, Level 2 detectors factory-calibrated for mercury, sulfur dioxide and chlorine are available. The approach to be taken by the EETD in regard to several of these 17 chemicals has not yet been decided.

Colourimetric methods of Level 2 complexity are known for 10 of these chemicals. On the assumption that we could adapt these methods for use with the HACH kit spectrophotometer, development work in this area is scheduled to proceed after April, 1984.

Existing Level 2 analytical capability for the water and soil mediums is restricted to water alone, and only encompasses water-soluble inorganic chemicals. Our efforts will be directed towards extending the application of HACH technology to the analysis of organic priority chemicals in water and soil as well as to the analysis of inorganics in soil. Simplified extraction procedures and apparatus must first be developed. While most inorganic priority substances and several organic priority chemicals can be extracted from soil with water, many organics of interest would have to be extracted from soil with an organic solvent.

In Table 2, applicable soil situations involving organic chemicals for which solvent extraction would be required prior to analysis are identified as being of lowest development priority. The same low priority has been assigned to water situations involving stable, non-reactive organic chemicals for which no potential colourimetric methods of analysis are known at this time.

The author's projected schedule for Level 2 analytical development in terms of the number of situations identified in Table 2 is summarized below in Table 3.

TABLE 3
PROJECTED SCHEDULE FOR DEVELOPMENT OF LEVEL 2
ANALYTICAL CAPABILITY FOR EETD PRIORITY CHEMICALS

	Cumulative Number of Substances			Cumulative Percentage of Substances		
Methodology by	Air	Water	Soil	Air	Water	Soil
April, 1984	56	59	0	77	47	0
April, 1985	66	105	67	90	83	58
April, 1986	>66	126	115	>90	100	100
No Projected Date	7	-	-	10	-	-

There is little doubt that the number of situations considered to be within the potential capability of Level 2 analytical systems will change, particularly in the uncharted regions of water and soil analysis, as development actually proceeds. However, it is also quite certain that the existing and potential spill monitoring capabilities associated with the OVA, HNU and HACH systems provide a high degree of coverage for the EETD priority chemicals list.

These systems also score well in terms of satisfying other essential requirements for Level 2 analysis. Existing EETD Level 2 systems are expected to develop into valuable and essential components of a comprehensive chemical spill response capability.

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PRACTICAL APPLICATIONS OF CONVENTIONAL AERIAL PHOTOGRAPHY TO HAZARDOUS WASTE SPILL EVALUATION

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The objective of this paper is to discuss the applications of conventional aerial photography to spill evaluation. As can be seen from the list of remote sensing techniques in Section 1, conventional aerial photography is only one of the many airborne techniques available. It is however, the most readily available, inexpensive, and easily interpreted technique, and can provide a wide variety of information applicable to the evaluation of hazardous materials spill.

1. REVIEW OF REMOTE SENSING TECHNIQUES

Remote sensing in its broadest sense includes the collection of any images, trace recordings, numerical counts, etc., by devices located remotely from the object of interest. Present capabilities confine us primarily to the recording of the following:

- electromagnetic energy
- radioactive decay processes other than gamma and x-rays which are included in the electromagnetic spectrum
- acoustical energy
- magnetic fields
- gravitational fields

The systems which enable us to record this information can be classified as follows:

I. Electromagnetic Spectrum (See Figure 1) --

   A. Recording of reflected energy from surfaces illuminated by sunlight, moonlight, artificial light (flash bombs).

      1. Conventional Photography

         a. Ultraviolet
         b. Black and white
         c. Color
         d. Infrared
         e. Narrow band
         f. Special film/filter combinations

        2. Spectroscopy

   B. Recording of reflected energy from surfaces illuminated by lasers (very narrow band).

   C. Recording of induced fluorescence in minerals and vegetation

   D. Recording of gamma and x-ray emissions

   E. Recording of reflections from surfaces illuminated by radio spectrum energy (radar)

   F. Recording of energy emitted as a function of temperature and emissivity (thermal imagery)

II. Radioactive Decay Products -- natural or induced, (alpha and beta particles, neutrons, protons)

III. Acoustical Spectrum -- measurement of reflected acoustical (pressure) waves from irradiated surfaces (sonar, seismic method)

IV. Magnetic Field -- measurement of magnetic fields using magnetometers

V. Electrical Field -- measurement of electrical fields using resistivity methods

VI. Gravity Field -- measurement of gravity using airborne gravimetry

2. CONVENTIONAL PHOTOGRAPHY

Because conventional photography is easily accessible and applicable to spill evaluation studies, the remainder of this paper will deal with the acquisition, use, and evaluation of this type of aerial image gathering. Types of conventional aerial photography applicable to spill evaluation include:

I. Mapping Photography -- Stereographic with scales of 1:7200 to 1:120,000 most commonly available

   A. Black-and-white
   B. Conventional color
   C. Color infra-red

II. Vertical Wide-Angle Photography

   A. Enviro-pod -- flown at altitudes of 250 to 12,000 feet (approximate scales of 1:1000 to 1:48,000, the scale increases with distance from the center of the photo as a result of wide-angle lens distortion).

      1. Conventional color
      2. Color infra-red
      3. High resolution black-and-white

B. Optical bar panoramic photography - flown at an altitude of 60,000 feet (approximate scale at the center of photo is 1:30,000)

   1. Color infra-red -- most optical bar imagery is flown with color infra-red due to its haze-cutting ability. This is an important factor with high-altitude photography.

   2. Conventional color

   3. High resolution black and white

III. Oblique Angle Photography

Part of Enviro-pod two-camera systems in which one lens is forward looking, 45° from vertical. Conventional color is used almost exclusively.

IV. Video Imagery

In the experimental stage; designed to provide rapid response to urgent requests for aerial imagery.

The most accessible photographs are black-and-white, vertical, available from the U.S. Department of the Interior, U.S. Geological Survey, and other sources. These are available for the 1930s to the present, usually with scales of 1:20,000 and 1:60,000. The format is 9" x 9" and the prints are from negatives of the same size. Each photo covers an area of 3 or 9 miles depending on scale. The photos are taken at appropriate intervals to provide stereo coverage of the entire area in question. Aerial photographs of selected areas are available from the National Aeronautics and Space Administration (NASA). These have scales of 1:60,000 and 1:120,000 on 9" x 9" prints. Each of these prints covers an area of 9 or 17 square miles. The larger-scale photography is more useful for spill studies, as the areas in question are usually measured in acres rather than square miles. Nine inch x nine inch format color, and infrared photographs, with scales of 1:7200 to 1:20,000 may be specially commissioned through the U.S. Environmental Protection Agency or private companies.

Enviro-pod photographs are taken by means of a self-contained, panoramic, two-camera reconnaissance system designed to be secured to the Cessna 172 aircraft. This system can provide vertical and forward-looking color or black-and-white photos with high resolution. This imagery is available through the U.S. Environmental Protection Agency. Because Enviro-pod photos are taken with a wide angle lens, considerable distortion occurs away from the center of the photographs, and they are not normally used for stereo work. However, the central portions of the photos may provide partial stereo coverage. Enviro-pod photography can be acquired more quickly and cheaply than mapping photography because the equipment required is much less elaborate. Because the scale is usually large, Enviro-pod photography is very useful for the study of small areas associated with most spill site studies.

For special purposes, such as early detection of vegetative stress, narrow-spectrum and multispectral imagery may be commissioned from private aerial photography companies. These systems require the use of various films and filters to image very narrow wavelength (70 to 400 A) bands of the visible, ultraviolet, and infrared spectra. Multispectral imagery associated with the NASA Skylab Program is available from the EROS Data Center in Sioux Falls, S.D., but is of limited use due to its small scale.

Oblique photographs have fewer applications than the previously mentioned photos because they provide no stereo coverage and the scales vary widely within a single picture. However, they are extremely easy to take and can provide data not available from ground level.

3. APPLICATIONS

Conventional aerial photography may be applied to spill studies for the acquisition of the following:

A. Base maps

B. Surface drainage patterns and directions

C. Identification of ground surface materials, including bogs, gravel, exposed bedrock, etc.

D. Bedrock type and competency

E. Land use

F. Vegetation types and vegetative stress

G. Population density

H. Selection of sampling points

Most areas of the United States have been photographed by the U.S. Department of the Interior more than once during the past 50 years. In many cases, three or more series of photos exist. This allows the investigator to evaluate environmental factors as they existed at different times in the past. The ability to evaluate progressive changes in environmental factors using "archival" imagery can provide a wealth of data to the investigator.

3.1 Base Mapping

Aerial mapping photography is required for base mapping because of the minimal distortion of ground surface characteristic of this type of photography. If the study area is large, it may be necessary to construct a photomosaic. This is done by taking every 9" x 9" photo in a consecutive series and carefully matching landmarks as the photos are taped or stapled to a rigid board. The remaining photos are used for stereographic examination of the mosaic. If the study area is small, a single 9" x 9" photograph may be sufficient to cover the entire area, and an enlargement of the photograph may be necessary. The photograph or photomosaic is then covered with acetate. No marking should be done directly on a photograph. All landmarks, including roads, railroads, lakes, and large buildings, are marked on the acetate. It is useful to locate all water wells on the base map, as important data, including the locations of water table, bedrock surface, and ground surface elevations, are tied to such points. All subsequent mapping of environmental factors is done using the same photo or photomosaic, so that the scale remains constant and factor maps can be superimposed. The base maps show past and present accessibility to the spill area either by road or railroad.

3.2 Surface Drainage

Surface drainage is easily mapped using stereo mapping photographs, and should be mapped to show as much detail as possible. Surface drainage patterns are strongly influenced by the nature of unconsolidated materials and bedrock types and structures. Stream flow is often controlled by folds and planar structures such as faults and joints within bedrock, as well as by the type of rock. Hard, resistent igneous, and metamorphic rocks are characterized by drainage patterns different from those of flat-lying or dipping sedimentary rocks. This information is very important in site evaluation work, as contamination often migrates within bedrock, and knowledge of bedrock structures is critical. Strong structural control of drainage patterns often indicates that bedrock is near the ground surface. This information is useful in evaluating the bedrock surface configuration, which is another factor that controlls migration of contamination within groundwater.

A very disorganized drainage pattern indicates the presence of surface deposits having very low permeability. This would indicate a low likelihood of rapid downward migration of contaminants into groundwater.

If no drainage pattern is present, precipitation is being immediately absorbed by porous materials such as loose sand and gravel, and contaminants are probably migrating very quickly through the overburden.

Surface water is often a conduit for contaminant migration. Therefore, a knowledge of past and present surface drainage downstream of a spill, with special attention to lakes, ponds, and streams used for domestic water supply or recreation is essential.

Changes in tone or color within a surface water body may indicate the influx of contaminated water.

3.3 Identification of Surficial Deposits

The nature of the unconsolidated materials at and near the ground surface will control the rate at which contaminants migrate downward to the groundwater. Aerial photographs contain many indicators of the nature of surface deposits. Section 3.2 discusses the relationship between surface drainage and overburden permeability. Bogs and swamps are easily distinguished in photographs by their tone and vegetation patterns. These features are characteristically underlain by two to twenty feet or more of impermeable organic silts and peat which readily adsorb heavy metals and organic contaminants slowing down or preventing their off-site migration. Examination of archival imagery may indicate areas of swamps, bogs, and lake bed deposits which are now industrial or residential areas.

Sand and gravel deposits have high reflectivity and are characterized in photographs by light tones where they are exposed at pits and road cuts. Glacial deposits are easily distinguished by their geomorphology. Kames and eskers, consisting primarily of permeable sand and gravel, are easily identified as sinuous or mounded topographic highs on flat or rolling plains. The plains are often underlain by glacial outwash or ground moraine deposits containing significant amounts of silt and clay resulting in low permeability. Other types of surface deposits can be distinguished by their topographic or surface drainage patterns. These include:

- o Impermeable laterite clays associated with karst areas;
- o Permeable sand and gravel beach deposits; and
- o Eolian or wind-generated deposits consisting of sands and silt.

3.4 Bedrock Types and Competency

As discussed earlier (Section 3.2), bedrock types often control surface drainage patterns.

Bedrock types also generate characteristic landforms such as the "valley and ridge" structure of the Appalachians which results from folded sedimentary strata. A good textbook on geomorphology will describe in detail the relationships between rock types, drainage patterns, and landforms.

The competency of the underlying bedrock is dependent upon the amount of fracturing and faulting in the rock. Weathering will reduce the competency of exposed rock surfaces by alteration along the fractures usually to a depth of five to ten feet. These exposed rock surfaces may later be buried by sedimentary deposits. Evidence of shallow buried rock surfaces can often be detected in aerial photos, and extensive fracturing and faulting will be evident in fracture trace analysis.

3.5 Land Use

The types of contamination present at a spill site are the result of the past and present land use of the site. Archival aerial imagery is an extremely valuable and very often the only available source of past land use data. As mentioned in Section 2, imagery dating from the 1930s is available from the EROS Data Center in Sioux Falls, South Dakota. The National Cartographic Information Center in Reston, Virginia (part of the United States Geological Survey) has developed a computerized system that helps users determine what archival aerial photos exist for a given area. This system is called the Aerial Photography Summary Record System (APSRS). If coordinates for a site are provided, APSRS will generate data regarding image scale, date of coverage, film type and format, sensor class, cloud cover, and other factors describing available archival imagery. Some of the important land use factors to be analyzed in archival as well as current photography are discussed in Sections 3.6 through 3.8.

3.6 Vegetation Types

Pesticides are a major group of hazardous materials having a very widespread occurrence. Although the use of many of these compounds has been banned for many years, they are very persistent in the environment and are often detected in areas where they are not anticipated. To determine the original sources of pesticides, it is often necessary to examine archival imagery. Pesticides can usually be traced back to agricultural areas which are easily identified in archival photos, even though the area of concern may have been used for industrial purposes for the past several decades. Wetlands are easily identified in air photos because of the flat, low vegetation which characterizes them.

Many types of vegetation are adversely affected or stressed by the presence of chemicals in the soil or groundwater. The effects may range from death of the plant to changes in leaf structure. These effects result in changes in the reflectivity of the foliage of the plant which are in many cases readily detectable in color or false color infrared imagery. The patterns of vegetative stress will often indicate the extent of a spill. Research has been done using very narrow land imagery (< 20 bands) to detect very small amounts of vegetative stress. Narrow bands in the green portion of the spectrum have been used to detect small amounts of stress due to the presence of metals (primarily copper) in soil. An example of the opposite of vegetative stress is the increased growth of algae resulting from phosphate pollution of surface water. This type of reaction is readily seen in air photos.

3.7 Population Density

The major concern of most spill site studies is what effect the hazardous materials will have on the people living in the area. The quickest method to determine in what ways a spill may impact local population is the use of recent aerial photographs. Once the surface water drainage patterns, evidence of vegetative stress, bedrock geology, and other environmental factors have been assessed, it is simple to determine the number of residences, factories, etc., which are located downgradient of a site and to estimate the population at risk.

3.8 Selection of Drilling and Sampling Locations

If further characterization of a spill site is required, aerial photos can be used effectively to select borehole and monitoring well locations, and surface water and soil sampling locations. Once all of the environmental factors have been mapped on overlays as suggested in Section 2, choosing locations is greatly simplified.

3.9 Summary

There are many applications of aerial photography to the evaluation of spill sites. The purpose of this paper is to create an awareness in those who do not use them on a daily basis of the range of applications of aerial photographs. This paper is not meant to be an exhaustive treatise on the subject but to encourage the use of a readily available, time- and cost-effective technique applicable to many aspects of environmental investigation and evaluation.

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Enviro-Pod Imagery - Seeing is Believing. United States Environmental Protection Agency, Office of Research and Development, Washington, D.C. (For further information, call the director of Remote Sensing Division at 702-736-2969, or the chief of the Environmental Photographic Interpretation Center at 703-347-6224, or write to Environmental Monitoring and Support Laboratory, Warrenton, Virginia, 22186)

The Aerial Photography Summary Record System - Send name, address, and telephone number to:

National Cartographic Information Center
United State Geological Survey
507 National Center
Reston, Virginia 22092
Telephone: 703-860-6045

The EROS Data Center - To place an order or inquire about the availability of data, contact:

User Services
EROS Data Center
Sioux Falls, SD 57198
Telephone: 605-594-6511, Ext. 151
(The EROS information booklet contains a good list of other sources of information)

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VEHICLE-PORTABLE SYSTEMS FOR MULTI-MEDIA ANALYSIS AT CHEMICAL SPILL SITES

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INTRODUCTION

The mandate of Environment Canada's Environmental Emergencies Technology Division (EETD) includes responsibility for developing and coordinating federal programs aimed at achieving technologically sound and effective response capabilities for spills of environmentally hazardous substances. Orginally formed in 1972 as the Environmental Emergencies Branch (EEB), EETD's research and development activities have, until recent years, focused primarily on the oil spill problem, particularly with respect to the arctic marine environment. While federal initiatives in this area continue, a comprehensive program to develop chemical spills response capabilities was launched in 1980 and is known as the Chemical Hazard Emergency Countermeasures (CHEC) Program.

Roughly 90% of hazardous chemical spill incidents involve a single substance. The substance or substances involved in a spill incident can usually be identified from evidence at the scene or from shipping documents. While the substance and perhaps even the spill volume may be known, rapid implementation of the correct response measures (which may include evacuation of the area, shutting down water treatment plants, etc.) requires (1) a knowledge of the chemical, physical, toxicological and environmental properties of the substances involved, and (2) rapid and sufficiently accurate determination of air, water, and soil concentrations of the chemicals in the vicinity of the spill site. A well known example illustrating the need for preparedness in these areas is the MacGregor derailment incident of 1980. Several days passed before reliable measurements of vinyl chloride concentration levels in air were obtained.

The authors have been contracted to continue development on two levels of the analytical component of the CHEC program. This paper is intended to serve as a summary of (1) the concepts upon which the analytical program is based, (2) the current development status of EETD vehicle-portable analytical systems for spill site use, and (3) our projection of future development possibilities at this level of analytical sophistication.

ANALYTICAL PROGRAM CONCEPTS

General Concept

One of the first tasks in the development program was an assessment of existing analytical capability in terms of potential applicability to spill monitoring. Based on criteria of portability, accuracy, and complexity, existing capability was divided into five levels, as shown in Table 1. Levels 1, 2 and 3 were considered most appropriate for spill monitoring. This paper focuses on the development of Level 3.

TABLE 1
EETD DESIGNATION OF ANALYTICAL LEVELS

Level	Description	Portability	Coverage	Status
1	Small detector system (usually colourimetric, e.g., Drager tubes)	Pocket-portable	Approx. 100 substances	Several commercially available units
2	Electronic detector systems (meters)	Person-portable	Perhaps 1000 substances	Development required
3	Computer-controlled instruments with pre-developed software.	Vehicle portable (small van)	Perhaps 10,000 substances	Development required
4	Mobile laboratories	Towable on good roads	As many as preparations are made for	Several prototypes exist, not very useful for rapid spill work in remote areas
5	Fixed laboratories	Not portable	As above	Existing and not very useful for spill work

Level 3 Concepts

In the concept development stage of the analytical program it was recognized that Level 1 and Level 2 analytical systems could not detect and/or quantitate certain substances in some media, and did not possess analytical capability for multi-substance spills. In order to achieve comprehensive spill monitoring capability it is necessary to develop a third, more sophisticated level of on-site analytical capability to complement and supplement Level 1 and 2 capabilities. Level 3 analytical capability will not be necessary in the majority of spill situations. Level 3 capability is seen as being necessary or desirable in the case of major spills, multi-substance spills, spills involving particularly toxic substances, and spills involving substances of complex and/or variable composition or formulation.

The development of Level 3 analytical capability is based upon the following basic concepts: 1) to render portable, in a small van, analytical systems normally considered as fixed laboratory instruments, 2) to modify, adapt, and develop hardware and software for selected systems so that these systems may be used to generate accurate on-site results by operators lacking the specific skills and knowledge typically required for the operation of sophisticated analytical instruments, and 3) the selected analytical systems will possess potential capability for all priority substances of interest in all media.

Level 3 systems possess inherent capability for higher accuracy compared to Level 1 and Level 2 systems. By specifying microprocessor-based instrumentation for Level 3, it is possible to develop chemical data bases for hazardous substances of interest, and user-friendly software which will allow for identification and quantitation of hazardous chemicals in all media by semi-skilled operators.

Priority Substances List

In order to focus the development of analytical capability on appropriate targets, a priority list of 150 chemical substances or groups was developed by the EETD. This priority list is specifically tailored to the current spill situation in Canada. Priority hazardous substances are listed in Table 2.

TABLE 2

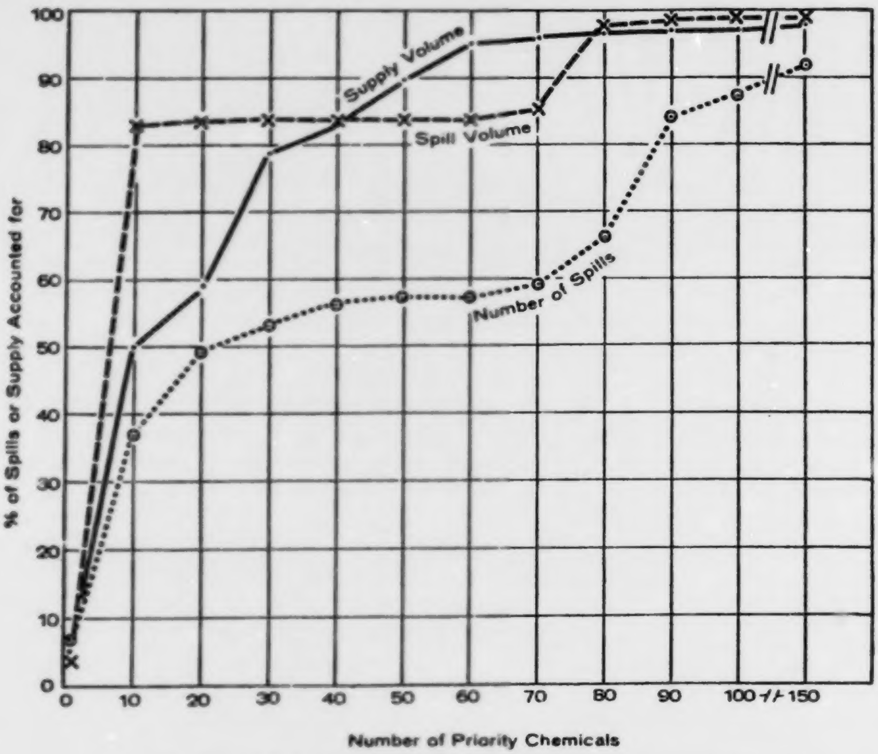
LIST OF PRIORITY HAZARDOUS MATERIALS FOR THE
ENVIRONMENTAL EMERGENCIES TECHNOLOGY DIVISION
THE 50 HIGHEST PRIORITY CHEMICALS
(in alphabetical order)

Acetic Acid
Acetic Anhydride
Ammonia
Ammonium Nitrate
Ammonium Phosphates
Benzene
Butyraldehydes
Calcium Chloride
Calcium Oxide/Hydroxide
Carbon Dioxide
Chlorine
Cyclohexane
Ethylbenzene
Ethylene
Ethylene Dichloride (1,2-Dichloroethane)
Ethylene Glycol
Ethylene Oxide
Ferric Chloride
Formaldehyde
Hydrogen Chloride/Acid
Hydrogen Fluoride/Acid
Hydrogen Sulfide
Mercury
Methanol
Morpholine
Naphtha
Natural Gas
Nitric Acid
Phenol
Phosphoric Acid
Phosphorus
Potash (Potassium Chloride)
Propylene
Propylene Oxide
Sodium Chlorate
Sodium Chloride
Sodium Hydroxide
Sodium Hypochlorite
Sodium Sulfate
Styrene (Monomer)
Sulfur
Sulfur Dioxide
Sulfuric Acid (and Oleum)
Tetraethyl Lead
Toluene
Urea
Vinyl Chloride
Xylenes
Zinc Sulfate
2-Ethylhexanol

THE SECOND GROUP OF PRIORITY CHEMICALS
(100 substances or groups)

Acetone
Acetylene
Acrylonitrile
Adipic Acid
Aluminum Chloride
Aluminum Hydroxide
Aluminum Sulfate
Aminocarb Pesticide (Matacil)
Ammonium Chloride
Ammonium Sulfate
Arsine
Barium Sulfate
Benzoic Acid
Borax
Boric Acid
Butanols
Butylene
Calcium Carbide
Calcium Carbonate
Calcium Hypochlorite
Calcium Phosphate
Caprolactam
Carbaryl
Carbofuran Pesticides
Carbon Disulfide
Carbon Tetrachloride
Chlordane
Chloroform
Copper Sulfate
Cresols
Dicamba
Dichlorobenzene
Dimethyl Ether
Dimethyl Terephthalate
Dinoseb
Diphenylmethane-4,4'-Diisocyanate
Ethanolamine
Ethanol
Ethylene Dibromide
Fenitrothion
Fluorochloromethanes
Formic Acid
Hydrazine
Hydrogen Peroxide
Hydrogen
Ispropanol
Ispropylbenzene
Latex
Lead Chromate
Lead Oxides
Magnesium Hydroxide
Malathion
Maleic Anhydride
Methyl Ethyl Ketone
Methyl Isobutyl Ketone
Methyl Methacrylate
Methylamines
Methylene Chloride
MCPA
n-Hexane
Nitrilotriacetic Acid
Nitroglycerine
Nonyl Phenol
PCBs
Pentachlorophenol
Pentaerythritol
Perchloroethylene
Phthalic Anhydride
Potassium Hydroxide
Potassium Sulfate
Propylene Glycols
Sodium Aluminate
Sodium Arsenite
Sodium Borohydride
Sodium Carbonate
Sodium Cyanide
Sodium Dichloroisocyanurate
Sodium Dichromate
Sodium Hydrosulfite (Dithionite)
Sodium Phosphates
Sodium Silicates
Sodium Sulfite
Sulfuryl Chloride
Tall Oil
Terephthalic Acid
Terphenyls
Titanium Dioxide
Triallate Pesticides
Trichlorfon Pesticides
Trifluralin Pesticides
Trinitrotoluene
Turpentine
Vinyl Acetate
Yellow Cake
Zinc Chloride
Zinc Oxide
1,1,1-Trichloroethane
1,3-Butadiene
2,4-D (2,4-Dichlorophenoxyacetic Acid)
2,4-Toluene Diisocyanate

Figure 1 illustrates the correlation between the number of spills, spill volume, and supply volume (production plus importation for the 150 priority chemicals. Certain substances of high chronic toxicity and widespread environmental concern, such as PCBs, have been included in the list despite low rankings in terms of supply and spill volume. Since a higher percentage of small volume spills of such substances tend to be reported to environmental authorities relative to lower-profile chemicals, a sharp rise is observed in the spill number curve between 80 and 90 on the horizontal axis.



Ability of Priority Chemicals to Account for the Maximum Amount of Spills and Chemical Supply

Figure 1. THE ANALYSIS OF THE TOP PRIORITY CHEMICALS

As seen from Figure 1, the first ten chemicals alone account for 37% of the number of spills, 50% of the supply volume and 83% of the spill volume. By extending the number of chemicals to 150 we account for over 90% of the reported spills and well over 90% of the spill volume.

EETD LEVEL 3 ANALYTICAL CAPABILITY

Review of Existing Level 3 Analytical Systems

Having developed Level 3 concepts, as well as the priority chemicals list, the EETD proceeded to assess the potential application of commercially available analytical instrumentation to spill site use. As a result of this review, three microprocessor-based systems were selected by the EETD for development as Level 3 systems. These systems consisted of a gas chromatograph (GC), an ultraviolet/visible (UV/VIS) spectrophotometer, and an infrared (IR) spectrophotometer. Brief descriptions of each system follow.

Gas Chromatograph

A Perkin-Elmer (PE) Sigma 2000 model microprocessor-controlled gas chromatograph was selected as a Level 3 system. This instrument is shown in Figure 2.

The Sigma 2000 GC is of modular design which allows convenient access to the components for ease of maintenance, repair, and modification (e.g. exchange of detectors or injectors). The Sigma 2000 is presently equipped with a PE model HS-6 Head-Space Analyzer, Figures 2 and 3, a manually-operated heated gas sampling valve, a photoionization detector (PID), and a flame ionization detector (FID). An electron capture detector (ECD) is also on hand for possible use but cannot be installed alongside the other detectors, as the GC is only designed to accomodate two separate detectors.

The head-space analyzer will be used for direct analysis of organic priority chemicals in water and soil. By automatic sampling of head-space vapour under controlled conditions the need for extensive sample preparation (extraction, clean-up, concentration) is eliminated (Figures 4 and 5). The gas sampling valve will allow for analysis of a known, reproducible volume of contaminated air from samples collected at the spill site in plastic (fluorocarbon) sampling bags.

The present PID/FID detector configuration complements the Level 2 air monitoring detector systems (HNU and OVA systems) and should be suitable for most field applications. The available ECD, while selective for halogenated chemicals such as pesticides and PCBs, may be inherently too sensitive to be of general utility for spill site applications. Furthermore, since the PID is an essentially non-destructive detector, the effluent from this detector can be directed to the FID, allowing for contaminant identity confirmation without the difficulties associated with splitting the GC effluent stream across two detectors.

The Sigma 2000 GC has been interfaced to a PE model 3600 data station which is capable of real-time data acquisition and post-run data manipulation (Figures 6 and 7). The data station can handle data from two detectors simultaneously. With appropriate programming (BASIC), the two detector response ratio for a given compound can be calculated and compared to a laboratory-compiled data bank for priority chemicals.

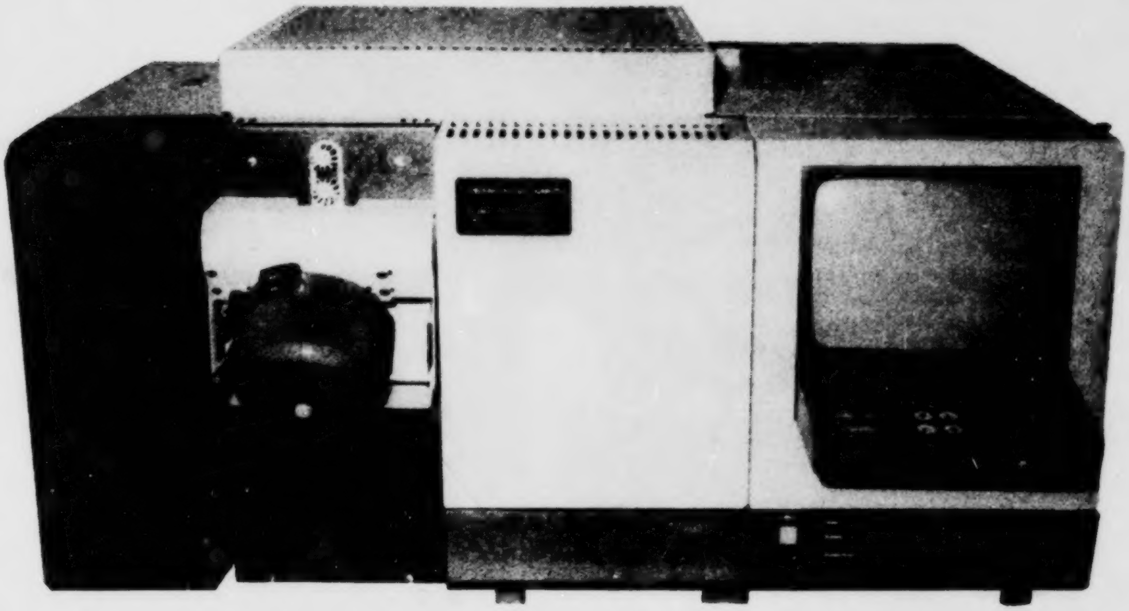
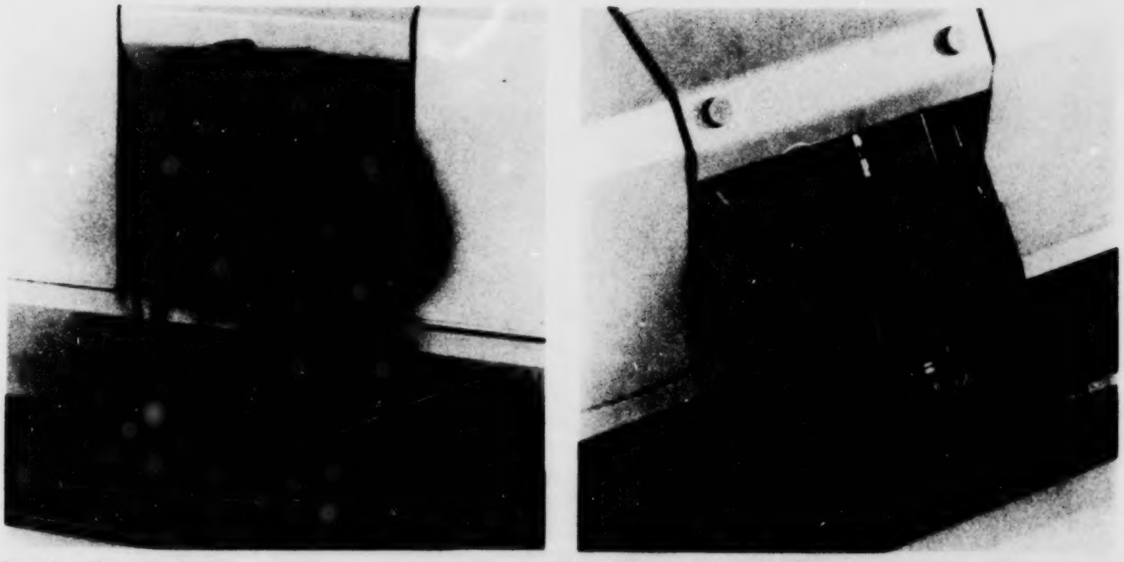


Figure 2. SIGMA 2000 GAS CHROMATOGRAPH



Inserting the sample vial

Sampling needle with spring-loaded septum. The sampling system is in the change position

Figure 3. HS-6 HEAD-SPACE ANALYZER

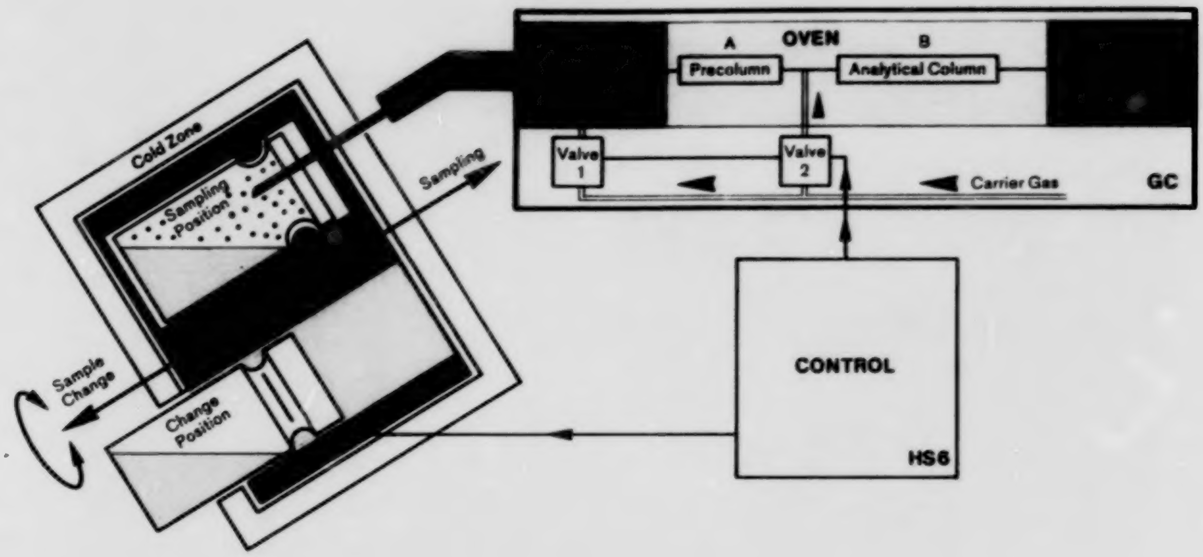
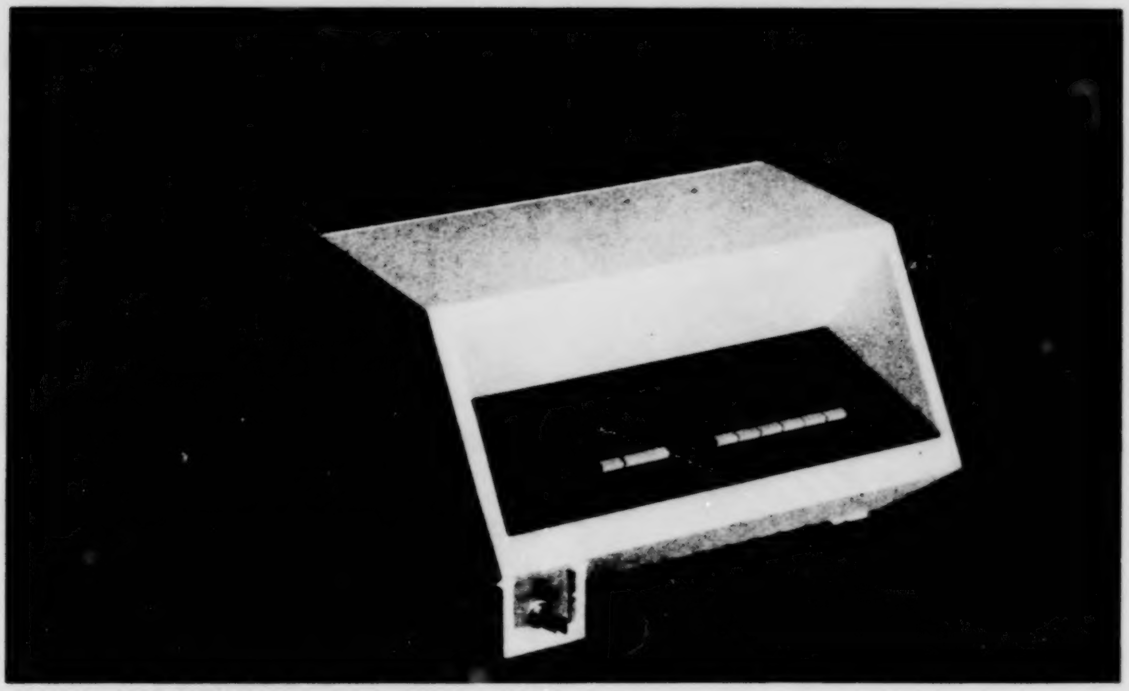

A
OVEN
B
Precolumn
Analytical Column
Valve 1
Valve 2
Carrier Gas
GC
Cold Zone
Sampling Position
Sampling
Sample Change
Change Position
CONTROL
HS6

Figure 4. HS-6 AND SIGMA 2000 CONFIGURATION



HS6 Control Unit includes timers and thermostat

Figure 5. HS-6 CONTROL UNIT

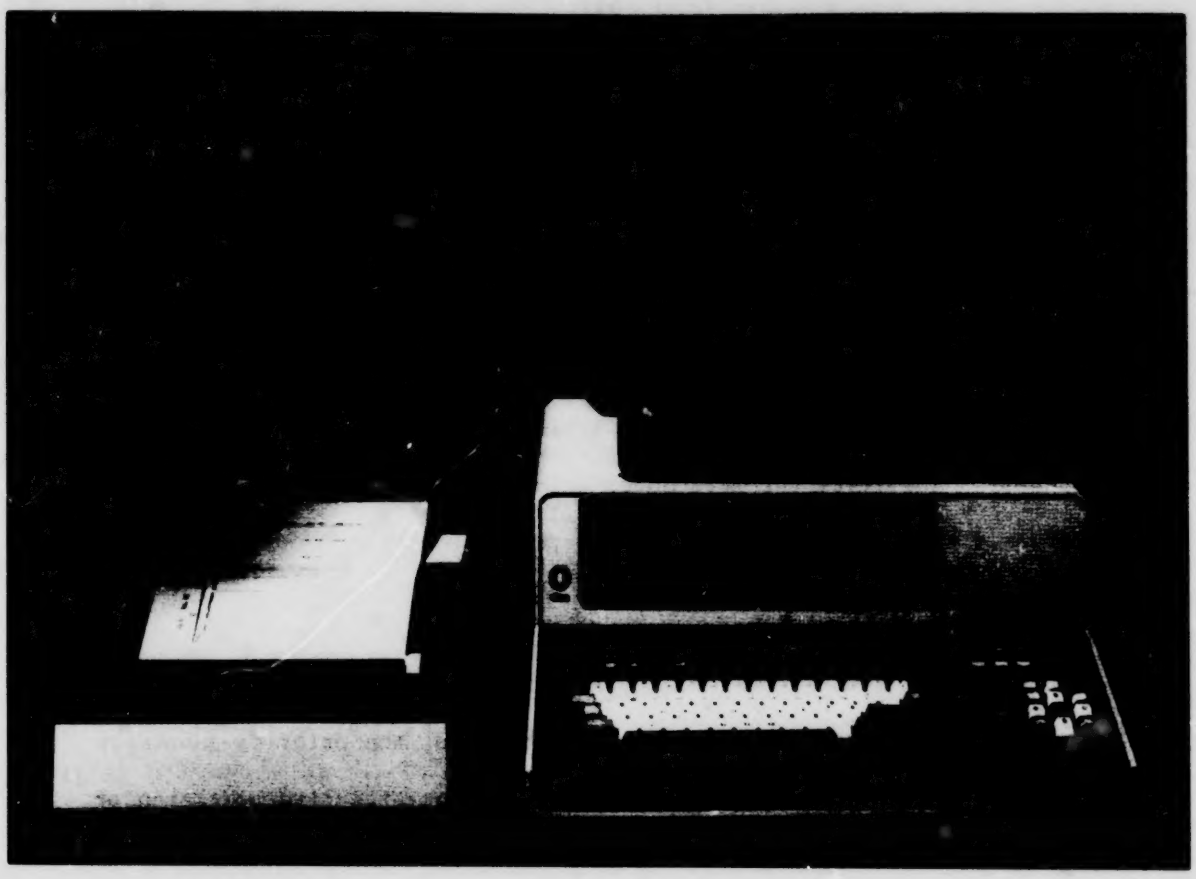


Figure 6. MODEL 3600 DATA STATION AND MODEL 660 PRINTER

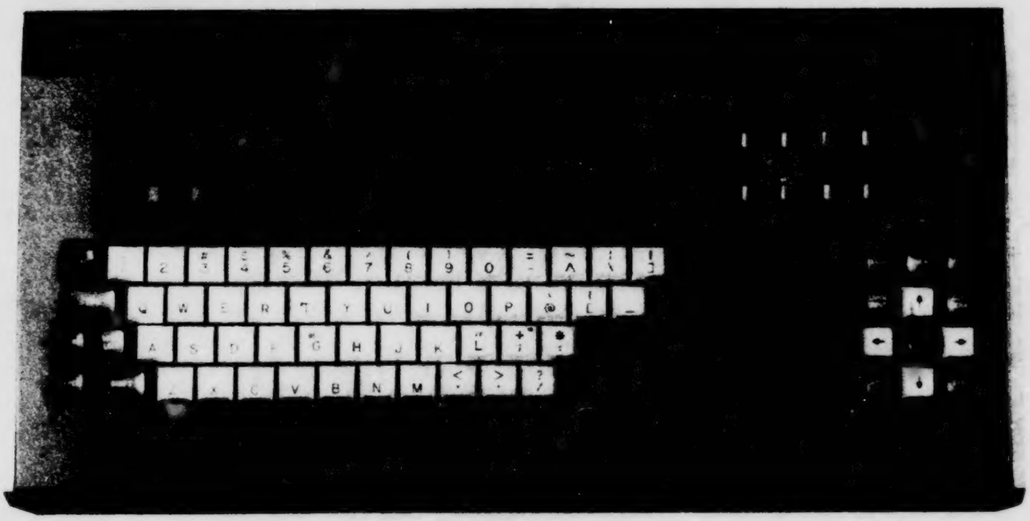


Figure 7. MODEL 3600 DATA STATION KEYBOARD

UV/VIS and IR Spectrophotometers

To complement and supplement GC analytical capability, the EETD has selected the PE model 683 IR Spectrophotometer and the PE model 552 UV/VIS Spectrophotometer as Level 3 systems. These instruments are shown in Figures 8 and 9. Level 3 software developed for these systems by another contractor requires interfacing the instruments to a TRS-80 Mark III computer for data analysis.

The IR system will find greatest application in the analysis of spill site air samples, while the UV/VIS system is expected to be most useful for the analysis of priority substances in the water and soil matrices. These analytical techniques are non-destructive, allowing for subsequent GC analysis of a sample if concurrent analysis is not possible or practical. The UV/VIS and IR systems are envisioned as providing priority chemical identity confirmation capability for substances which are amenable to GC analysis. As supplementary techniques, the UV/VIS and IR systems must have capability to identify and quantitate substances which cannot be handled by GC techniques.

The features required for the Level 3 UV/VIS and IR computer systems are as follows:

1) real-time acquisition of data from the spectrophotometer.
2) ability to identify contaminants by comparing sample spectra to a library of laboratory-compiled standard spectra for priority substances.
3) quantitation capability once the identity of the priority substance has been determined by the system.
4) user-oriented computer software to allow for effective operation of the systems by operators lacking extensive technical backgrounds.

Current Level 3 Development Status

The Sigma 2000 GC has only recently been installed in the EETD laboratory in the configuration (selected injectors, detectors, optional accessories) required for development work. All system components are now operating to the manufacturer's specifications, but Level 3 software development has not yet begun. Present efforts are focused on making the modifications necessary to place the FID in-series with the PID so that a simultaneous dual detector system can be used to identify sample components.

At least for the present time, packed columns will be used for the separation of sample components. If higher resolution or greater sensitivity is required in the future, the Sigma 2000 is configured with capillary column capability. However, several technical problems would have to be overcome before a capillary column system could be used effectively for spill site applications.

Preliminary development work on the UV/VIS and IR computer systems has been carried out by another contractor. A complete evaluation of the systems' merits, as they stand, is currently being conducted before further development work is pursued. The evaluation will examine such aspects as: ease of use, accuracy of identification, accuracy of quantitation, and amenability to field use.

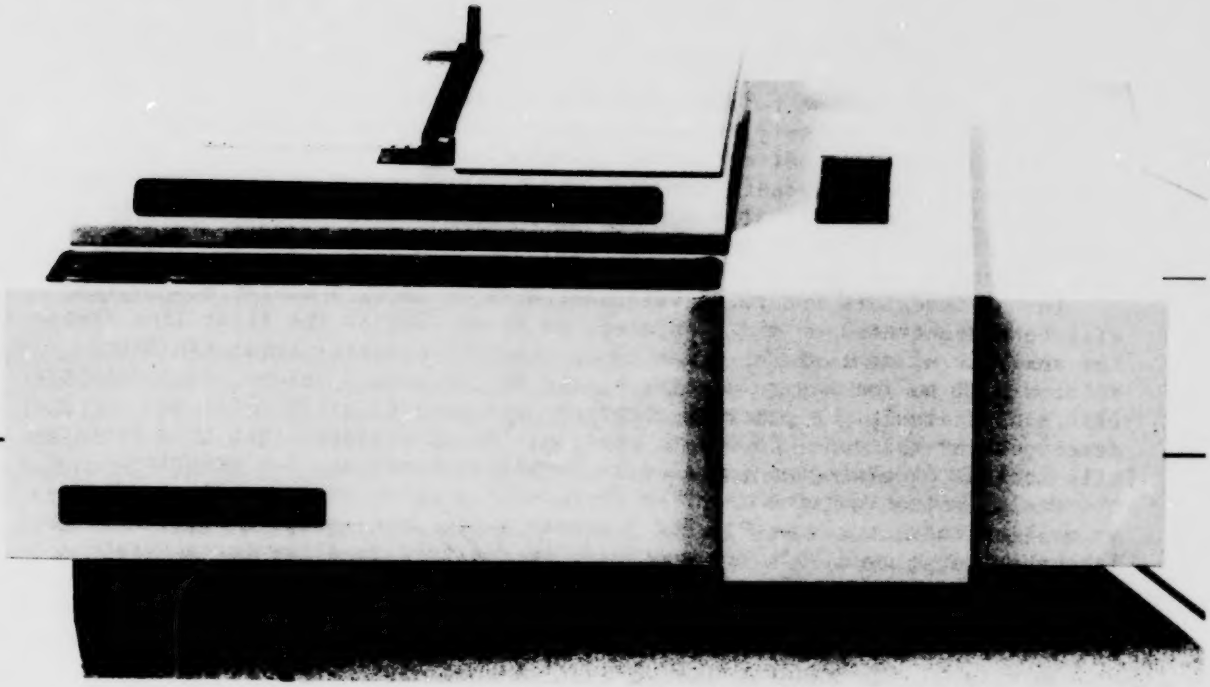


Figure 8. MODEL 683 INFRARED SPECTROPHOTOMETER

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Figure 9. MODEL 552 ULTRAVIOLET/VISIBLE SPECTROPHOTOMETER

Since documentation on the systems is vague and incomplete, the evaluation process is very time-consuming. The present systems appear to have serious inherent deficiencies. The software is not sufficiently user-oriented, to understate the case, as to fulfill the concept requirements for Level 3 systems. It also appears that the acquired spectra for EETD priority chemicals are of low resolution, and may not be adequate for identification and quantitation purposes.

In the immediate future, development work on Level 3 analytical systems will be concentrated on the GC system, as it is seen as the first line system for analysis of most of the organics on the EETD priority chemicals list. Efforts will be focused on setting up the GC for packed column, dual detector (PID/FID) analysis. A priority chemical data base (library) will be developed for the model 3600 data station. It is expected that this library will include chromatographic relative retention time data for priority chemicals (retention time relative to carefully selected internal standards), as well as characteristic PID/FID response ratio data for each substance. The laboratory-developed software must also be designed to allow for accurate quantitation when any of several possible injection techniques are used.

The course of future development on the Level 3 UV/VIS and IR systems is difficult to predict at this time. Once the current evaluation process has been completed, the direction of development will be decided. Several software packages are now available to allow for use of the UV/VIS and IR spectrophotometers with the PE 3600 data station. If major changes in the present systems are required before they can be considered field-ready, then the more recently available software packages may be incorporated into these Level 3 systems. Since the GC, UV/VIS, and IR systems are all capable of stand-alone operation, and interfacing of these instruments to the 3600 data station does not appear to be a problem, this latter approach may be the most expedient.

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PCBs SPILL AT FEDERAL PIONEER LIMITED's REGINA PLANT

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D. A. Fast, P. Eng.
Saskatchewan Environment

INTRODUCTION

In 1976 an underground pipe carrying Inerteen 70-30 from an outdoor storage tank to the indoor manufacturing facilities ruptured at the plant of Federal Pioneer Limited (FPL) in Regina, Saskatchewan. (Figure 1) The exact amount that was lost is not known, but company records indicated that from 6,800 to 21,000 litres of Inerteen 70-30 were unaccounted for. This material contains about 70 per cent polychlorinated biphenyls (PCBs) and about 30 per cent tri- and tetra- chlorobenzenes (TCBs). Some small accidental spills that occurred during the plant's past operations may have contributed to additional soil contamination around the site. Following the 1976 spill, FPL reportedly drilled holes in the spilled area and recovered some of the PCBs, but a large portion remained in the ground.

Remedial measures undertaken by FPL in 1976 included paving the surface of the spilled area with asphalt and the installation of eavestroughs on the building. These interim measures were approved by Saskatchewan Environment as temporary means of containment, because of the lack of other options for removing and disposing of the large volume of contaminated soil. Between 1976 and 1978, soil samples were collected at the site by Saskatchewan Environment and Environment Canada to evaluate the suitability of the measures that had been taken.

In the fall of 1978, widespread public concern was expressed about the possible contamination by PCBs of ground water in Regina. In response to these concerns, the Government of Saskatchewan asked the National Research Council of Canada to establish an *ad hoc* panel of scientists to extensively study the site and to prepare a report recommending remedial work.

The NRC panel completed its work and a fully documented report was issued to the province in January, 1980. Areas of the FPL site which were contaminated with PCBs were identified (Figure 2). Based on the results of their investigation, the panel concluded that there was not an immediate threat to the ground water. The remedial containment measures taken had not, however, been entirely effective and, there was a need to immediately contain the surface contamination due to the threat to surface water quality. There was also a need, over the longer term, to prevent downward and lateral migration of PCBs to protect the water quality of the Regina aquifer system.

In view of the uncertainties regarding predictions of future migration of PCBs from the FPL site and the possible impact that such movement might have on water quality in the Regina Aquifer System, the panel made a general recommendation to remove all of the most highly contaminated soils from the FPL site. More specifically in its January 30, 1980, summary report, the panel made recommendations for remedial action in four areas:

A. Actions to restrict the surface and near surface migration of PCBs;
B. Actions to restrict the deep surface migration of PCBs;
C. Requirements for storage facilities;
D. Monitoring requirements for the FPL site.

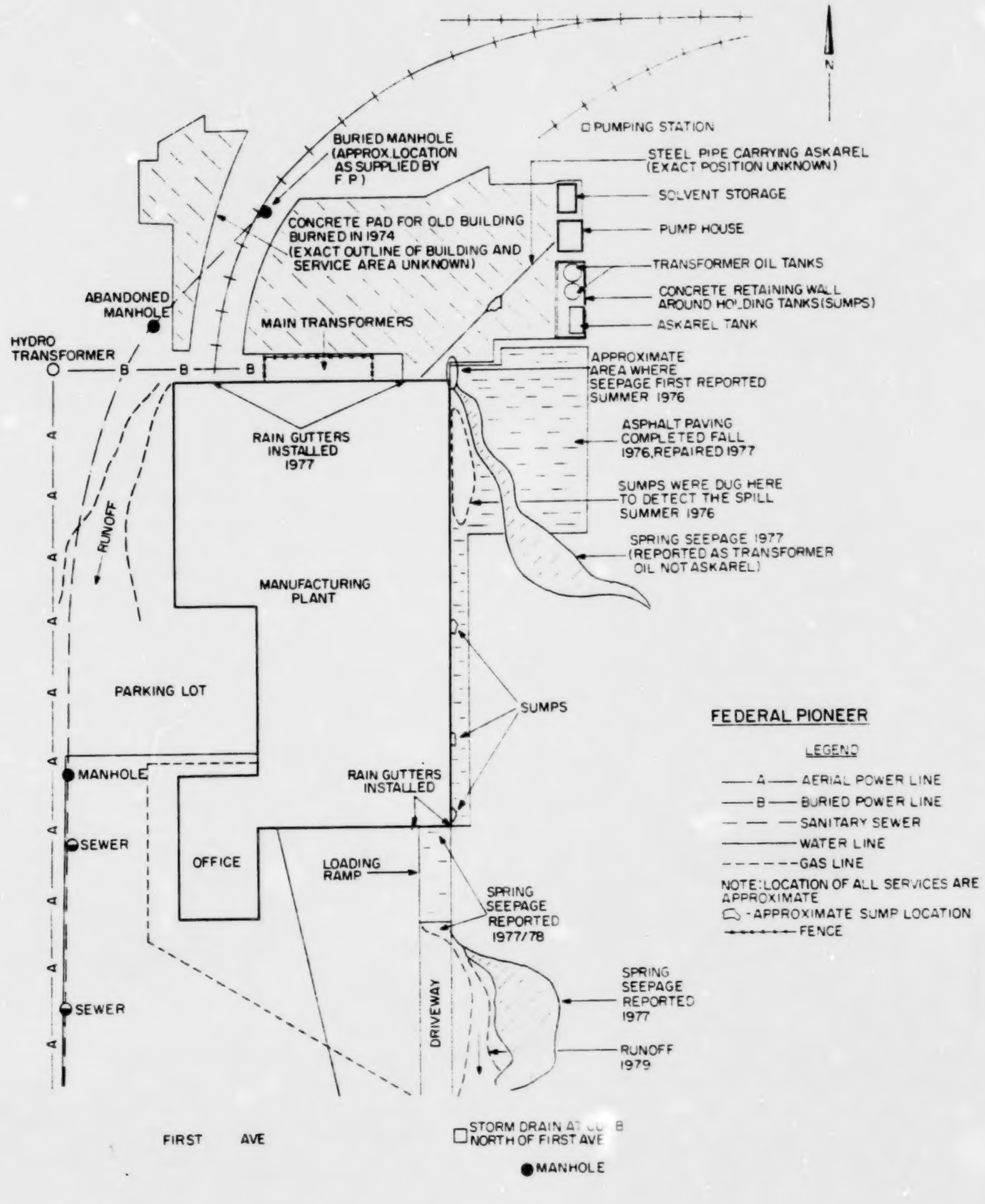
N
PUMPING STATION
BURIED MANHOLE
(APPROX.LOCATION
AS SUPPLIED BY
F P)
STEEL PIPE CARRYING ASKAREL
(EXACT POSITION UNKNOWN)
SOLVENT STORAGE
PUMP HOUSE
CONCRETE PAD FOR OLD BUILDING
BURNED IN 1974
(EXACT OUTLINE OF BUILDING AND
SERVICE AREA UNKNOWN)
TRANSFORMER OIL TANKS
CONCRETE RETAINING WALL
AROUND HOLDING TANKS (SUMPS)
ASKAREL TANK
ABANDONED
MANHOLE
MAIN TRANSFORMERS
HYDRO
TRANSFORMER
B
B
B
APPROXIMATE
AREA WHERE
SEEPAGE FIRST REPORTED
SUMMER 1976
RAIN GUTTERS
INSTALLED
1977
ASPHALT PAVING
COMPLETED FALL
1976, REPAIRED 1977
SUMPS WERE DUG HERE
TO DETECT THE SPILL
SUMMER 1976
RUNOFF
SPRING SEEPAGE 1977
(REPORTED AS TRANSFORMER
OIL NOT ASKAREL)
MANUFACTURING
PLANT
A
PARKING LOT
SUMPS
FEDERAL PIONEER
LEGEND
—A— AERIAL POWER LINE
—B— BURIED POWER LINE
— — — SANITARY SEWER
———— WATER LINE
- - - - - - GAS LINE
NOTE: LOCATION OF ALL SERVICES ARE APPROXIMATE
APPROXIMATE SUMP LOCATION
FENCE
MANHOLE
RAIN GUTTERS
INSTALLED
SEWER
OFFICE
LOADING
RAMP
SPRING
SEEPAGE
REPORTED
1977/78
SPRING
SEEPAGE
REPORTED
1977
SEWER
DRIVEWAY
RUNOFF
1979
FIRST AVE
STORM DRAIN AT CURB
NORTH OF FIRST AVE
MANHOLE

Figure 1 HISTORICAL SITE MAP

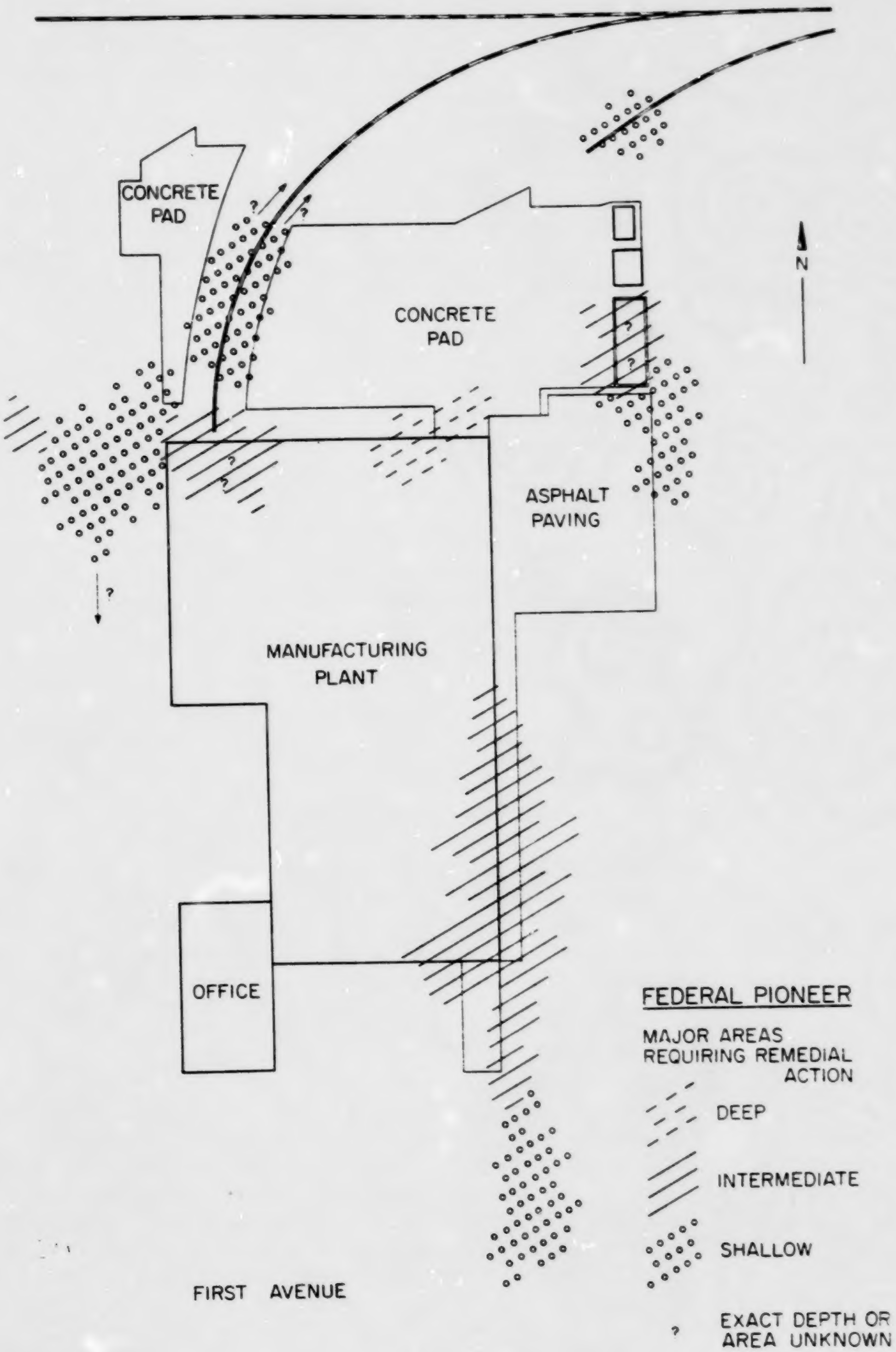
CONCRETE PAD
CONCRETE PAD
N
ASPHALT PAVING
MANUFACTURING PLANT
OFFICE
FIRST AVENUE
?
FEDERAL PIONEER
MAJOR AREAS REQUIRING REMEDIAL ACTION
DEEP
INTERMEDIATE
SHALLOW
EXACT DEPTH OR AREA UNKNOWN

Figure 2 MAJOR AREAS REQUIRING REMEDIAL ACTION

The panel also indicated that eventually the overall site should be cleaned up but not until adequate facilities are ready for safe storage or destruction of the PCBs in the contaminated soil.

REMEDIAL MEASURES PLANNING ACTIVITIES

In late 1979, a technical "Advisory Committee on the Regina PCB spill" was formed to oversee the remedial measures required at SPL site. The Committee members consisted of representatives from FPL, the City of Regina, Environment Canada and Saskatchewan Environment, as the Chairman of the Committee.

Detailed proposals by FPL and by consultants hired by Saskatchewan Environment were reviewed by the Advisory Committee. The Committee recommended the following measures be implemented:

(a) Shallow highly contaminated soil identified in four areas where materials had migrated off of FPL property should be removed and securely stored on FPL property;
(b) Recovery wells or sumps should be installed to remove water in the perched water table in the fill. Water removed should be securely stored at the site and properly disposed of at a later date;
(c) A bentonite slurry cutoff wall (barrier) should be constructed around the entire FPL site to a depth of 30 feet. The bentonite wall should go through the fill and 4-5 feet into the native clay;
(d) The eavestroughing on the FPL building should be completed;
(e) The entire surface area inside the cutoff wall should be sealed by lime modified, compact clay and a contoured asphalt covering; and
(f) An ongoing monitoring and site surveillance program should be implemented as soon as the interim remedial clean up measures were completed.

INTERIM CLEAN UP ACTIONS

In September, 1980, FPL agreed to comply with the recommendations made by the Technical Advisory Committee and a mutually acceptable clean up program was finalized shortly after. The program involved a series of co-ordinated measures to be undertaken immediately by FPL and it was anticipated that the work would be substantially completed during that year. Highlights of the site clean up program are presented below:

Surface Seal and Drainage

A survey was carried out to determine the topographic and structural features on the site, including the location of all services such as water supply, sewers, etc. The survey was used to design the surface seal and drainage system which would eliminate all potential infiltration of surface runoff from precipitation or other sources into the ground beneath the seal.

Areas which were already paved with concrete or asphalt were inspected and all cracks and damaged sections were repaired. All other areas which were not paved were graded to the gradient necessary to affect efficient surface runoff and, modified with lime. Finally, these areas were surfaced with approximately 100 mm of asphalt sub-base followed by 100 mm of asphaltic concrete. All junctions with buildings and structures were raised and sealed against the concrete surface. The entire surface area within the bentonite cutoff wall was sealed.

Explore and Delineate Limits of Plume

This work was performed in two stages. The first was to define the limits of the shallow areas of high contamination designated as areas 1, 2, 3 and 4 in Figure 3. The completion of this work was required before excavation of the contaminated soil on the adjoining properties could commence. The work carried out during the first stage included surface sampling, drilling and sampling in holes (Shelby tubes) up to 4 metres in depth and laboratory soil analysis for PCBs.

The second stage was to define the limits of the plume in the deeper areas within the boundaries of the property. This work was not performed until the seal had been completed and the perched water table had been nearly dewatered. Work carried out during this stage included deeper drilling and sampling of the Regina clays and Condie silts. Sampling and testing were carried out in stages in advance of the filling.

Excavation and Storage of Contaminated Material

Contaminated soils on the site and the adjoining properties, as shown on areas 1, 2, 3 and 4 in Figure 3, were excavated by means of a backhoe and removed to a storage area. The storage area is located between the plant building and the eastern boundary of the site. The area was raised during the sealing and paving operation and the subgrade clay was modified with lime and sealed with asphalt before the contaminated soil was placed on it. The excavated soils were spread on the prepared surface in layers and modified with lime. The area was finally sealed with the final seal and paving.

Slurry Bentonite Cutoff Wall

A slurry bentonite cutoff wall was constructed to contain the migration of PCBs. The vertical slurry cutoff wall was installed using the vibratory beam injection method to key into the relatively impervious Condie silt layer. A bentonite slurry mixture was pumped under controlled pressure to fill the cavity formed by the steel beam as the beam was withdrawn from the ground.

The cutoff wall was constructed along the lines shown on Figure 4 and extended from the surface to one metre into the top of the Condie silt layer (approximate 10 metres in depth and 75 mm in thickness) as shown in Figure 5.

Dewatering Wells

A system of shallow wells and sumps were installed in the granular fill overlaying the Regina clay to drain the perched water table and the contaminated water pumped out was securely stored for disposal.

During the whole clean up period, a consulting firm was retained by Saskatchewan Environment to maintain on-site surveillance, monitor and regularly report on the progress of the operation.

The 1980 Remedial Measures progressed slowly initially, but a major portion of the work was completed that year. The 1981 Remedial Measures consisted of the finalization of an interim storage area, the completion of the excavation of contaminated material from areas 1, 2 and 4, and the completion of the cutoff wall and paving.

LONG-TERM MONITORING

With the completion of the on-site PCB containment system, basically through hydraulic isolation, it is essential to monitor the containment

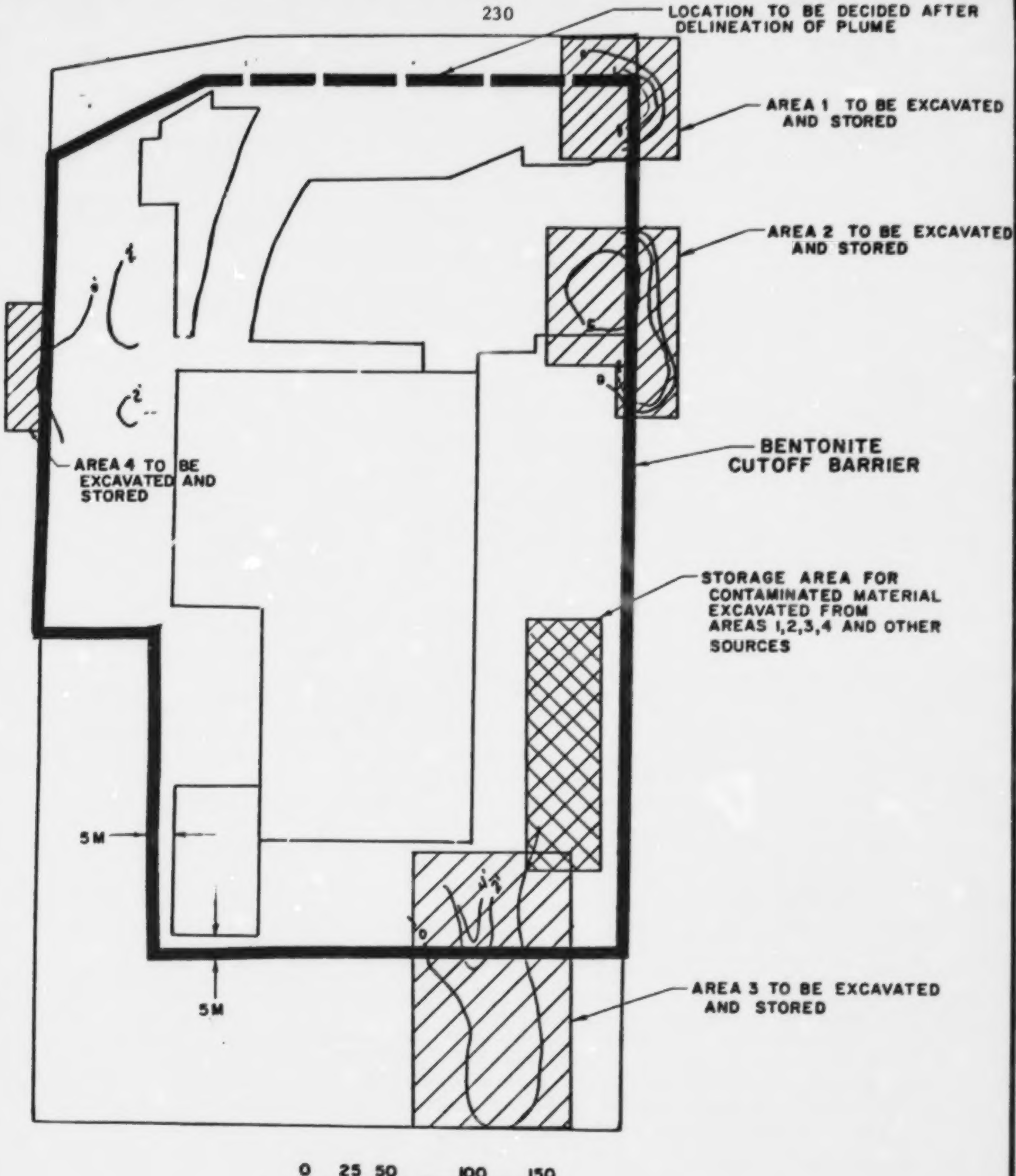
LOCATION TO BE DECIDED AFTER DELINEATION OF PLUME
AREA 1 TO BE EXCAVATED AND STORED
AREA 2 TO BE EXCAVATED AND STORED
AREA 4 TO BE EXCAVATED AND STORED
BENTONITE CUTOFF BARRIER
STORAGE AREA FOR CONTAMINATED MATERIAL EXCAVATED FROM AREAS 1,2,3,4 AND OTHER SOURCES
5M
5M
AREA 3 TO BE EXCAVATED AND STORED
0
25
50
100
150
SCALE (ft.)

Figure 3 AREAS OF EXCAVATION

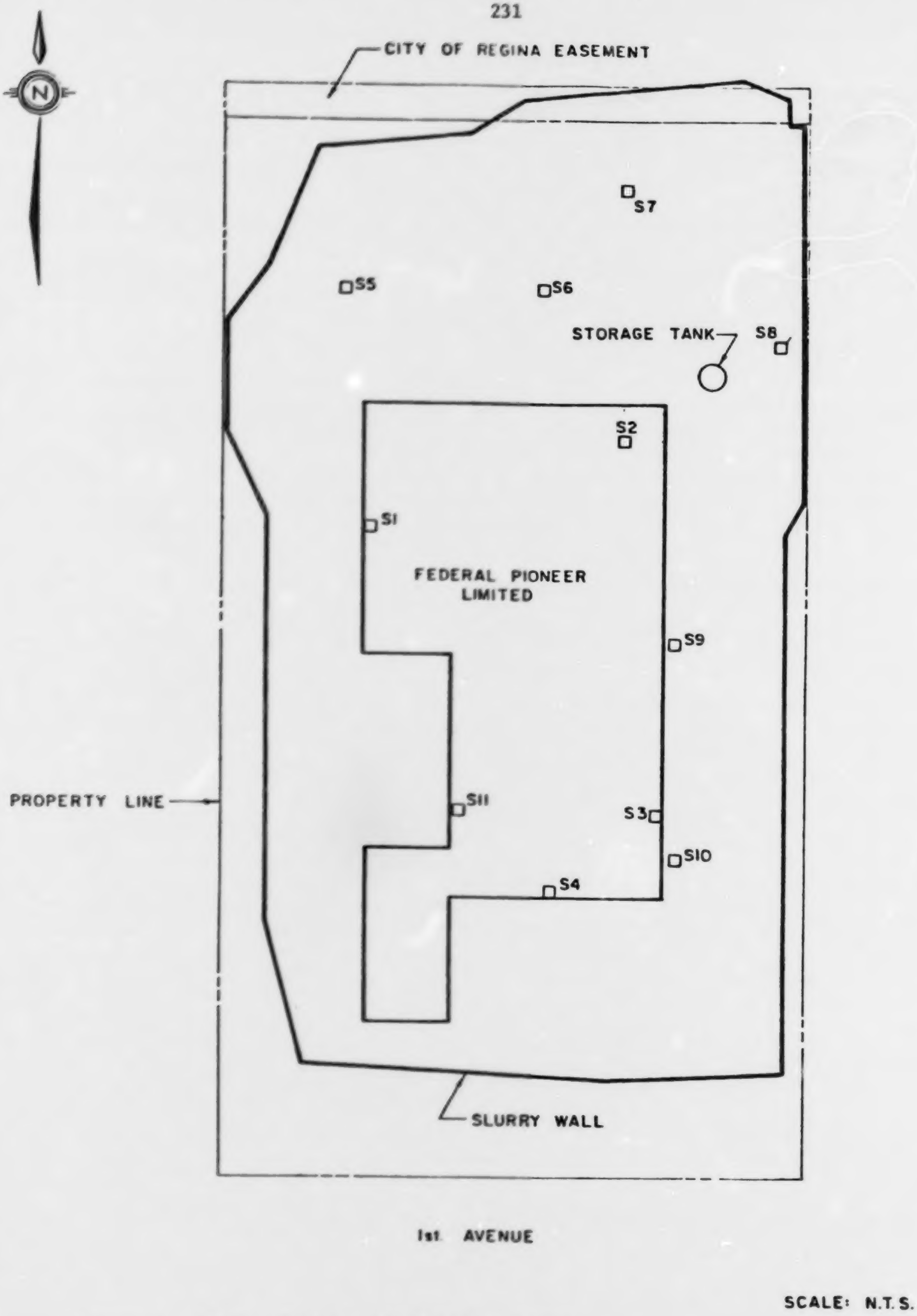
N
CITY OF REGINA EASEMENT
S7
S5
S6
STORAGE TANK
S8
S2
S1
FEDERAL PIONEER LIMITED
S9
PROPERTY LINE
S11
S3
S10
S4
SLURRY WALL
1st AVENUE
SCALE: N.T.S.

Figure 4 LOCATION OF SUMPS AND SLURRY WALL

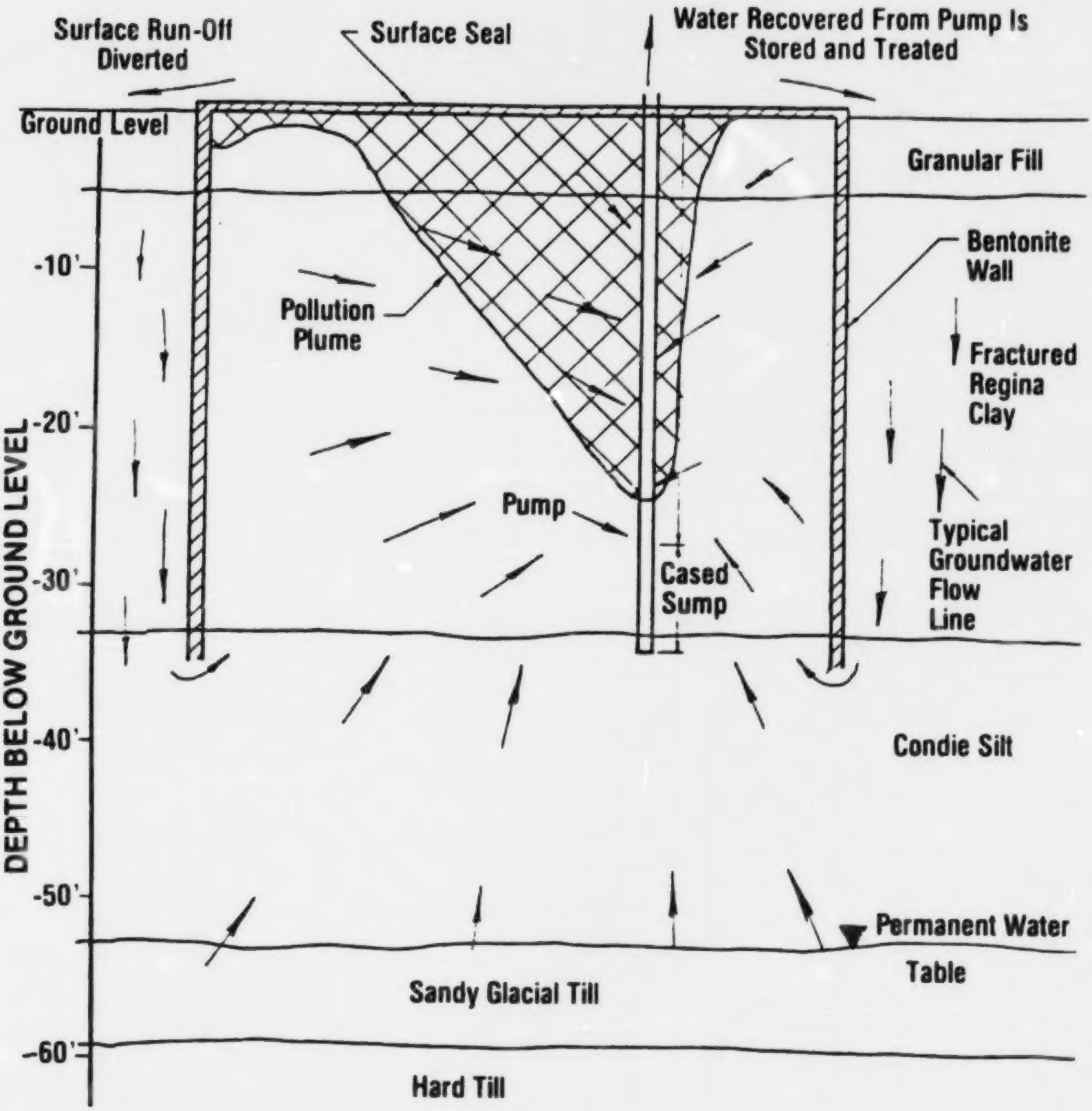
Surface Run-Off Diverted
Surface Seal
Water Recovered From Pump Is Stored and Treated
Ground Level
Granular Fill
-10'
Bentonite Wall
Pollution Plume
Fractured Regina Clay
-20'
Pump
Typical Groundwater Flow Line
Cased Sump
-30'
-40'
Condie Silt
DEPTH BELOW GROUND LEVEL
-50'
Permanent Water Table
Sandy Glacial Till
-60'
Hard Till

Figure 5 SECTION OF GROUND UNDER PLANT SHOWING HOW THE BENTONITE WALL AND PUMPS CHANGE THE FLOW OF GROUND WATER AND PREVENT THE SPREAD OF THE PCBs

structure in order to ensure that the system continues to function as designed. A long-term monitoring program was developed and implemented prior to the beginning of spring runoff in April, 1982. The program consists of the following:

Site Surveillance

The surface seal at the entire site was thoroughly inspected in spring and fall of 1982. Tension cracks at two locations were observed and resealed by the application of a liquid asphalt-sald mixture. Separation cracks between the concrete and asphalt surface structures had developed and they were sealed by the application of an asphalt emulsion slurry.

The eavestroughing system and surface drainage at the site were inspected during spring runoff and a heavy rainfall in September, 1982, and were observed to be performing satisfactorily.

Drums containing contaminated materials were stored on the east side of the building within the enclosed storage area. Inspection of these containers indicated that they were in good condition and no leaks have occurred.

An inspection of all sump and piezometer covers in September, 1982, found all covers to be in good condition and were providing a proper seal for the winter.

Surface Runoff Testing

Water samples collected during spring runoff and during a heavy rainfall in the summer of 1982 were analyzed for PCB content. The values were very low and ranged from 3 parts per billion (ppb) to less than 1 ppb.

Dewatering Programs

Up to December, 1982, a total of more than 70,000 gallons of water were removed from the eleven sumps, as shown in Figure 4. Higher than expected water levels in two sumps in the spring of 1982 (No. 7 and 8) were suspected to have been caused by a leak in the plant's water distribution system. A water pressure test was conducted and detected no leak in the system.

However, automatic pumping equipment was later installed in sump No. 7 and 8 to provide regular and consistent pumping. Water removed from the sumps was delivered to a 13,000 gallon storage tank and subsequently disposed of at an approved out of province location. It was estimated that approximately 40,000 to 65,000 gallons of perched water remained to be removed in the area of sump No. 7 and 8. To increase the pumping capacity, two additional sumps were installed in the spring of 1983 at the north end of the site within the deepest fill areas.

Piezometer Monitoring

A total of 65 piezometers have been installed at the site, of which 50 are within the surficial fill material and the remaining 15 are installed at deeper elevations to monitor the natural ground water table which remained relatively stable throughout the 1982 monitoring period.

During the 1982 monitoring period, water level readings from shallow piezometers installed at the site showed an overall decreasing trend within the fill areas. Twelve additional shallow piezometers were installed in July, 1982, to assist in evaluating the effectiveness of the cutoff wall and also to better determine the hydraulic gradients inside and outside the cutoff wall.

Deep Soil Sampling and Pore Water Extractions

The first deep test hole sampling program was performed during the 1982 monitoring period. This program consisted of: (a) deep test hole drilling; (b) collection of soil samples for PCB analysis; and (c) pore water collection within the Condie silt.

Four test holes were drilled in an area adjacent to the northeast corner of the building plant where the deepest PCB contamination is present. Soil samples were collected for the entire depth of the three test holes in the triangular set to determine geology and to provide soil samples for PCB analysis.

The centre hole within the triangular set was drilled into the Condie silt for the purpose of collecting soil and extracting sufficient pore water samples for PCB analysis.

Deep soil sampling data indicates that PCBs are generally confined to the Regina clay above the clay-silt contact, but low PCB concentrations were present within the upper fraction of the silt in the bottom samples of one test hole at a depth of 11 metres. Although PCBs were detected at a slightly greater depth during 1982 relative to that observed in 1979 and 1980, it is not thought that significant downward movement had occurred in that period.

The results from the 1982 monitoring program indicate that the dewatering is progressing satisfactorily and that the containment and investigation programs are fairly effective.

As previously noted, this monitoring program is an ongoing requirement at the FPL site. In order to assist FPL in finding a permanent solution, Saskatchewan Environment and Environment Canada are jointly attempting to identify current research and techniques that may be applicable to the PCB contamination problem at the FPL plant site in Regina.

In March, 1981, the Province of Saskatchewan enacted the Environmental Spill Control Regulations, which require the mandatory reporting and clean up of chemical spills, to ensure prompt remedial actions are undertaken in all spill events to protect the environment.

NEUTRALISATION ET ATTÉNUATION DES IMPACTS D'UN DÉVERSEMENT DE 3 600 TONNES D'ACIDE SULFURIQUE CONCENTRÉ

L. J. Moulins* et D. G. Pannell**

RÉSUMÉ

Lors du week-end du 5 et 6 juin 1982, le bris d'une vanne de drain laissait échapper d'un réservoir de 10 000 tonnes quelque 3 600 tonnes d'acide sulfurique à 93%. Le déversement s'est canalisé par le biais de l'usine d'épuration municipale, dans le premier des deux bassins de rétention du complexe minier de Mines Gaspé. La surverse du deuxième bassin forme la tête d'un tributaire d'une rivière à saumons, la rivière York.

Afin de protéger cette ressource biologique, une vaste opération de neutralisation de l'acide déversé a été entrepris avec succès. Le pH de la rivière York s'est maintenu normal et la majorité des métaux dissous a pu être précipitée dans le deuxième bassin de rétention.

L'impact écologique s'est limité à la partie supérieure de la rivière. A l'automne, les saumons adultes ont pu frayer en nombre suffisant pour assurer une bonne reproduction naturelle.

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1.0 INTRODUCTION

Mines Gaspé, filiale du groupe Noranda, est située à Murdochville, Québec (Canada), à environ 100 Km au Sud-Ouest de la ville de Gaspé.

Les opérations comprennent deux mines - ciel ouvert et souterraine -, deux concentrateurs, une usine de smeltage jumelée à une usine d'acide et, finalement, une usine de minerai oxydé et de cémentation. Les résidus miniers provenant des concentrateurs sont acheminés vers trois parcs à résidus où les déchets solides sont décantés tandis qu'une partie des eaux est recyclée vers les diverses installations du complexe minier. L'excédent d'eau se déverse dans la branche Sud de la rivière York, cette dernière étant une rivière à saumons de l'Atlantique (*Salmo salar*).

Mines Gaspé a toujours maintenue une attitude positive pour la protection de l'environnement et, de ce fait, possède son propre service de l'environnement. Ce dernier a élaboré un programme de suivi et de protection environnmentale très efficace et respectueux des milieux à protéger.

1.1 Agencement hydrologique des lieux (voir figure 1)

Le complexe minier et les parcs à résidus sont situés en amont de la rivière York et les eaux de procédées, après avoir décanté leurs solides, sont polies dans un étang à cet effet. Cet étang, ou bassin de récupération (2ième lac), a une capacité de 92 x 10^6 m^3 d'eau et est alimenté par un premier lac, artificiel, qui reçoit les eaux traitées de l'usine d'épuration municipale. Ce premier lac d'une capacité de 69 x 10^6 m^3 d'eau a comme tributaires deux ruisseaux nommés Copper et Porphyre. Finalement, un étang d'eau brute fait la jonction entre les ruisseaux et le premier lac. La figure 1 présente au lecteur le régime hydrographique situé en amont de la rivière York.

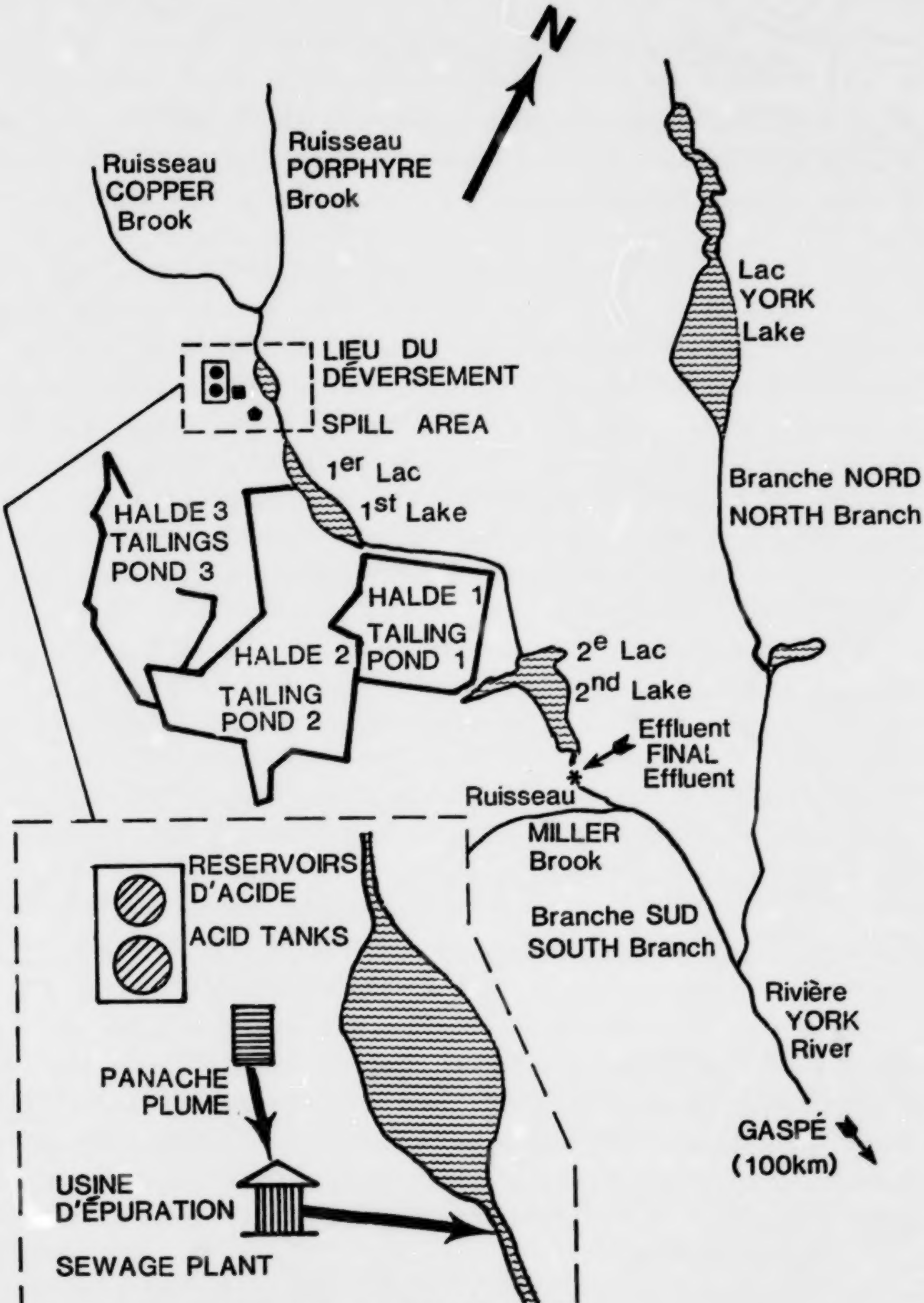
N
Ruisseau COPPER Brook
Ruisseau PORPHYRE Brook
Lac YORK Lake
LIEU DU DÉVERSEMENT
SPILL AREA
1er Lac
1st Lake
Branche NORD
NORTH Branch
HALDE 3
TAILINGS POND 3
HALDE 1
TAILING POND 1
HALDE 2
TAILING POND 2
2e Lac
2nd Lake
Effluent FINAL Effluent
Ruisseau MILLER Brook
RESERVOIRS D'ACIDE
ACID TANKS
Branche SUD
SOUTH Branch
Rivière YORK River
PANACHE
PLUME
GASPÉ (100km)
USINE D'ÉPURATION
SEWAGE PLANT
LIEU DU DÉVERSEMENT SPILL AREA

FIGURE I

1.2 Le déversement d'acide sulfurique

Au cours du week-end du 5 et 6 juin 1982, le bris d'une valve de drain sise au sous-sol de l'aire de chargement des camions citernes véhiculant l'acide, a laissé échappé quelques 3 600 tonnes d'acide sulfurique concentré à 93%.

L'acide concentré s'est facilement frayé un chemin dans le sol sous-jacent vers la canalisation des eaux usées et pluviales de la municipalité. Aucun changement en humidité ou coloration du sol n'était visible en surface. En somme, l'acide n'a pas fait apparition sur le sol. Après avoir atteint l'usine d'épuration, l'acide s'est évacué par le biais de la canalisation de surverse de l'usine municipale, ce, dans le ruisseau adjacent (Porphyre) quelque peu en amont du premier lac. Le médaillon "lieu du déversement" de la figure 1 schématise pour le lecteur le trajet du panache d'acide.

Le déversement a été détecté à la suite d'échantillonnages environnementaux réguliers. Les résultats analytiques révelèrent, entre autres, que l'eau du 1er lac offrait un pH 2 pour un degré d'acidité d'environ 1%.

La fuite fut aussitôt colmaté et le calcul de l'inventaire d'acide sulfurique à 93% présentait un déficit de quelque 3 600 tonnes. Les autorités gouvernementales furent avisées.

2.0 ATTÉNUATION DES EFFETS DU DÉVERSEMENT

Face à un déversement de cet ampleur, et de la fragilité du système écologique en jeu, les interventions de mitigation se doivent d'être rapides et efficaces. Toutefois un tel déversement n'est pas chose commune et aucun expert en ce domaine n'était disponible tant du côté des autorités gouvernementales que du groupe Noranda. Dès lors, Mines Gaspé décida de prendre en charge les opérations d'atténuation, ce, avec l'assentiment du Ministère de l'environnement du Québec.

Le plan d'intervention peut se résumer en deux étapes, soit une recirculation accrue des eaux contaminées vers les haldes des résidus miniers et le chaulage de l'eau acidulée à divers points stratégiques. Ces deux paliers d'intervention furent executés concurremment selon la description et la logique qui suit.

2.1 Recirculation des eaux contaminées

Le but de cette recirculation était de réduire, momentamément, le débit à la surverse du 2^{ième} lac et aussi de favoriser une neutralisation passive de l'eau dans les haldes à résidus.

Pour ce faire des pompes submersibles "Flight" furent installées à divers endroits et l'eau était pompée soit vers les haldes à résidus 1 ou 2. L'installation des pompes s'est fait concurremment à la pose de fils pour l'alimentation électrique et à la mise en place de tuyaux "Sclairpipe" pour acheminer l'eau qui serait éventuellement pompée. Certaine section de tuyau pouvait atteindre jusqu'à 300 mètres de longueur.

Dans un premier volet, l'effluent de l'usine d'épuration municipale était détourné. Cette eau était en somme la source d'entrée de l'acide dans le système hydrographique environnant. En effet, l'acide s'était frayé un chemin souterrain, puis, par infiltration, était entré dans la canalisation bétonnée qui alimente l'usine d'épuration en eaux usées. La pompe installée à cet endroit avait une capacité de 1 500 gpm et pompait presque entièrement l'effluent vers la halde à résidus 2.

Dans un deuxième volet, trois pompes installées dans le canal joignant le 1er et le 2^{ième} lac déviaient jusqu'à 5 000 gpm d'eau acidulée dans la halde à résidus 1.

Enfin, dans un troisième volet, deux pompes d'une station de pompage permanente, sise à la sortie du 2^{ième} lac, recirculait jusqu'à 5 000 gpm d'eau par le biais d'un des concentrateurs vers la halde 2.

Le pompage de ces quelque 11 500 gpm réduisait momentanément d'environ du tiers de débit normal de la surverse du $2^{ième}$ lac. Dans une telle période d'urgence, l'utilisation des haldes à résidus devenaient un atout. Ainsi, l'eau pompée se retrouvait dans d'immenses bassins dont le temps de rétention favorisait l'évaporation et, dans une certaine mesure, la neutralisation à cause du carbonate de calcium que renferme les résidus de Mines Gaspé à raison de 10% à 20%.

En plus de cette neutralisation naturelle, de la chaux hydratée était ajoutée aux 5 000 gpm recirculés du $2^{ième}$ lac vers un concentrateur qui, ensuite, était dirigée dans la halde 2. Cette halde reçevait donc un débit relativement élévé ayant un pH fluctuant entre 10 et 12.

Toutefois, il faut noter que la recirculation des eaux contaminées a été rendue possible grâce à l'arrêt des opérations de traitement du minerai.

2.2 Chaulage de l'eau acidulée

Simultanément au pompage, l'addition de neutralisant dans le réseau hydrographique en amont de la surverse du $2^{ième}$ lac constituait la pierre angulaire pour rétablir le pH de l'eau.

Les neutralisants employés ont varié de la soude caustique (NaOH dilué à 50%) à la chaux hydratée ($Ca(OH)_2$), en passant par du carbonate de soude ($Na_2(CO_3$) et de la pierre à chaux (70% $CaCO_3$).

Sauf pour la soude caustique qui était directement drainée des camions citernes, les autres neutralisants étaient épandus mécaniquement par les équipements disponibles sur place. Parmi ces équipements, notons une souffleuse à neige et des épandeuses mobiles du même type que celles utilisées pour épandre le sel sur les routes canadiennes en hiver.

L'ajout des neutralisants secs dans l'eau s'est fait aux points les plus turbulents afin de favoriser la réaction chimique. Les principaux points de déversement étaient situés à l'entrée et la sortie du 1^{er} et du

$2^{ième}$ lac où des épandeuses régularisaient le débit des neutralisants.

D'autre part, pour accélérer la neutralisation du $2^{ième}$ lac, une souffleuse à neige projetait dans l'eau de la pierre à chaux. Cette méthode fut rapidement raffinée au profit d'un tuyau troué de 10" cm de diamètre qui traversait en partie le $2^{ième}$ lac et dans lequel un lait de chaux hydratée était pompé. Ce tuyau était supporté par des flotteurs pour le maintenir en surface, et une vanne papillon fermait l'une des extrêmités. A l'autre bout, c'est-à-dire à la berge, une épandeuse déversait de la chaux hydratée dans un bassin creusé à même le rivage et le mélange chaux hydratée-eau était acheminé par une pompe submersible dans le tuyaux troué à un débit maximum de 1 000 gpm. Il est à noter que cette méthode fut très efficace malgré les difficultés d'installation.

Concernant la soude caustique, elle était directement déversée dans le sous-sol de l'aire de chargement des camions citernes où avait fuit l'acide lors du bris de la vanne de drain. Par ce geste nous voulions tenter de neutraliser in situ l'acide résiduel dans le sol. Quoique les résultats de cette action soient difficiles à estimer, nous sommes d'avis qu'elle a contribué à circonscrire le panache d'acide souterrain.

3.0 COMPORTEMENT PHYSICO-CHIMIQUE DE L'EAU

La section qui suit a trait aux changements physico-chimique de l'eau, induits par le déversement d'acide sulfurique, dans le système hydrologique récepteur.

Deux principaux paramètres seront évalués soit, le pH et le cuivre. Quoique d'autres métaux aient été présents dans l'eau lors de la fuite, le cuivre à cause de sa concentration et de sa toxicité sur la faune aquatique a retenu notre attention. Tant qu'au pH, sa fluctuation acidique ou alcaline sera un point de repère important afin de jauger l'état des espèces métalliques dissoutes ou solides.

3.1 Le pH (voir figure 2)

Règle générale, le pH normal de l'eau de la région varie entre 7 et 8 selon le cycle des saisons. La capacité tampon de l'eau est bonne due à une alcalinité relativement élevée causée par la présence de carbonates. Ces carbonates sont issus principalement des formations géologiques calcaireuses environnantes. La portion gauche (septembre 1975 - novembre 1979) de la figure 2 illustre pour le lecteur les fluctuations normales du pH dans le bassin de récupération (2 ième lac) situé à la tête de la branche Sud de la rivière York.

Lors de la fuite d'acide, le pH du 1er lac (voir figure 1) et du 2ième lac, d'un volume respectif d'environ 69 et 92 millions de mètres cubes d'eau, s'est graduellement abaissé. Ainsi, au début juin 1982 l'eau de surface du bassin de récupération a présenté un pH passant d'environ 7 à 3,5. Pour sa part, l'eau en profondeur a suivi, grosso modo, la même tendance sans toutefois s'abaisser au-delà de pH 4.

Sous l'action du chaulage, le pH s'est graduellement rétabli pour atteindre, au début juillet 1982, des valeurs avoisinantes 8. Toutefois, selon le produit neutralisant utilisé et son mode d'application, le comportement du pH a varié dans la colonne d'eau. Ainsi, la pierre à chaux (70% $CaCO_3$), appliquée en vrac à l'aide d'une souffleuse à neige, a eu un effet notable sur le pH de l'eau profonde du lac. Par contre, l'eau de surface n'a pratiquement pas offert de changement. Chimiquemment, nous pouvons attribuer à la pierre à chaux une augmentation de pH jusqu'à environ 7 de l'eau en profondeur. Pour l'eau de surface, la hausse du pH a surtout été notoire avec l'ajout de chaux hydratée pompée puis distribuée dans la partie médiane du lac. Cette montée de pH, pour l'eau de surface, a été observable à partir de la fin juin 1982. Par la suite, celui-ci a fluctué entre 8 et 10. La portion droite (juin - septembre 1982) de la figure 2 résume les résulats observés.

pH DU BASSIN DE RÉCUPÉRATION

(2nd LAKE)

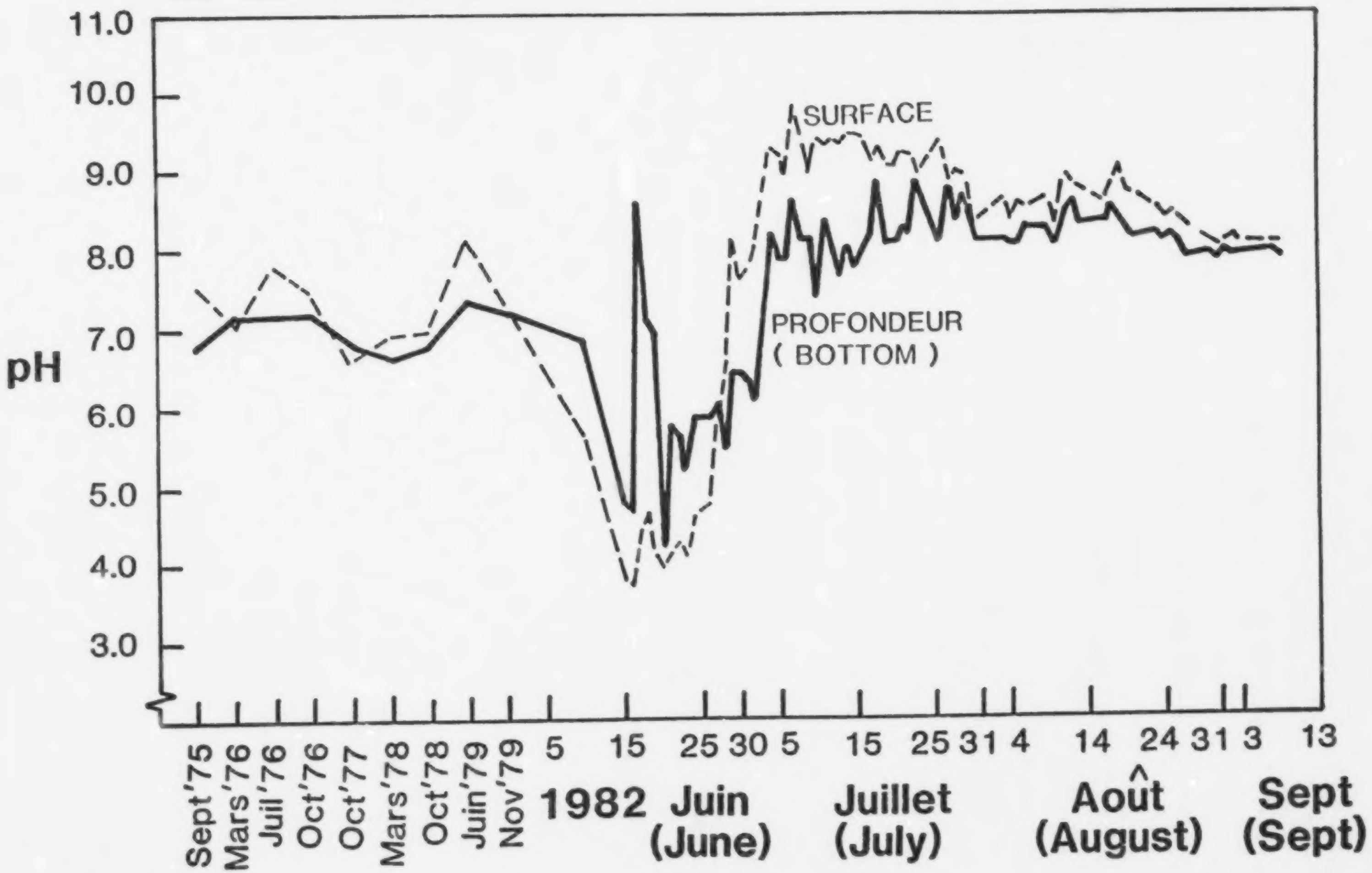

FIGURE 2

Il est à noter qu'à cette période de l'année une stratification thermique s'établit dans le bassin de récupération qui, par endroit, atteint jusqu'à 12 mètres de profondeur. Dès lors, nous croyons que la thermocline a influencé la distribution des valeurs de pH, ce, même sous l'effet d'un chaulage intensif. Cette ségrégation des valeurs de pH est d'ailleurs observable en temps normal (septembre 1975 - novembre 1979, figure 2) en offrant une condition légèrement plus acide en eau profonde qu'en surface. Toutefois, ce phénomène tend à s'estomper lors du brassage des eaux au printemps et à l'automne.

Concernant la hausse subite du pH en eau profonde vers le 15 juin 1982, elle a été induite par un mélange de pierre à chaux et de chaux hydratée qui avait été projeté à l'aide d'une souffleuse à neige dans le lac. Donc, la valeur de pH 9 observée est attribuable à la portion de chaux hydratée et non pas à la pierre à chaux seule.

Finalement, pour favoriser la précipitation complète des métaux dissous lors de la baisse de pH, ce dernier fut maintenu à un niveau supérieur à 8 jusque vers la mi-septembre 1982.

3.2 Le cuivre total et dissous

Le bassin de récupération, ou $2^{\text{ième}}$ lac, agit comme lagune de polissage aux eaux de surverse des haldes à résidus. Ainsi, la plupart des résidus solides sédimentent directement dans les haldes tandis que les particules plus fines, entraînées par l'eau de surverse des haldes, se déposeront dans le bassin de récupération. D'autre part, puisque Mines Gaspé exploite du minerai cuprique, la plupart des particules métalliques susceptibles de sédimenter dans les haldes ou dans le bassin de récupération sont composées de cuivre.

Nous nous attarderons maintenant au comportement in situ de ce métal lors du déversement d'acide sulfurique.

3.2.1 Le cuivre total et dissous à l'effluent final

L'effluent final du complexe minier est situé à quelques centaines de mètres en aval de la surverse du bassin de récupération et est positionné, pour le bénifice du lecteur, sur la figure 1.

Le site de l'effluent final est crucial en soi car il fait partie intégrante de la branche Sud de la rivière York au-delà duquel aucun contrôle sur la qualité de l'eau ne peut-être exercé. La portion gauche de la figure 3 présente au lecteur les variations normales du pH et du cuivre total et dissous, tandis que la portion droite, c'est-à-dire de juin 1982 à septembre 1982, exprime les mêmes paramètres sous l'effet du déversement et de sa neutralisation subséquente.

La concentration en cuivre totale varie normalement entre 0,2 mg/l et 0,3 mg/l, tandis que la portion dissoute fluctue aux environs de 0,15 mg/l. Concernant le pH, il se maintien entre 7 et 8. Les concentrations de cuivre durant les premiers six mois de 1982 montraient une amélioration par rapport à la même période en 1981.

Lorsque le pH a chuté dans le bassin de récupération, une dissolution du cuivre particulaire aussi bien dans la colonne d'eau que dans les sédiments de surface s'est produite. Dès lors et malgré l'ajout de neutralisant à la surverse du bassin de récupération, une concentraton éleveé de cuivre dissous s'est retrouvée à l'effluent final, ce, malgré un pH légèrement alcalin. Ainsi la pierre à chaux a réussi à maintenir le pH près de la neutralité sans toutefois précipiter efficacement le cuivre dissous.

Cependant, dès que de la chaux hydratée fut utilisée pour être appliquée par pompage au centre du bassin de récupération, le pH a rapidement atteint l'alcalinité voulu pour précipiter le cuivre dissous. D'ailleurs la figure 3 illustre éloquemment la relation inversement proportionnelle qui s'est établie au début juillet 1982 entre le pH et les

EFFLUENT FINAL
(FINAL EFFLUENT)

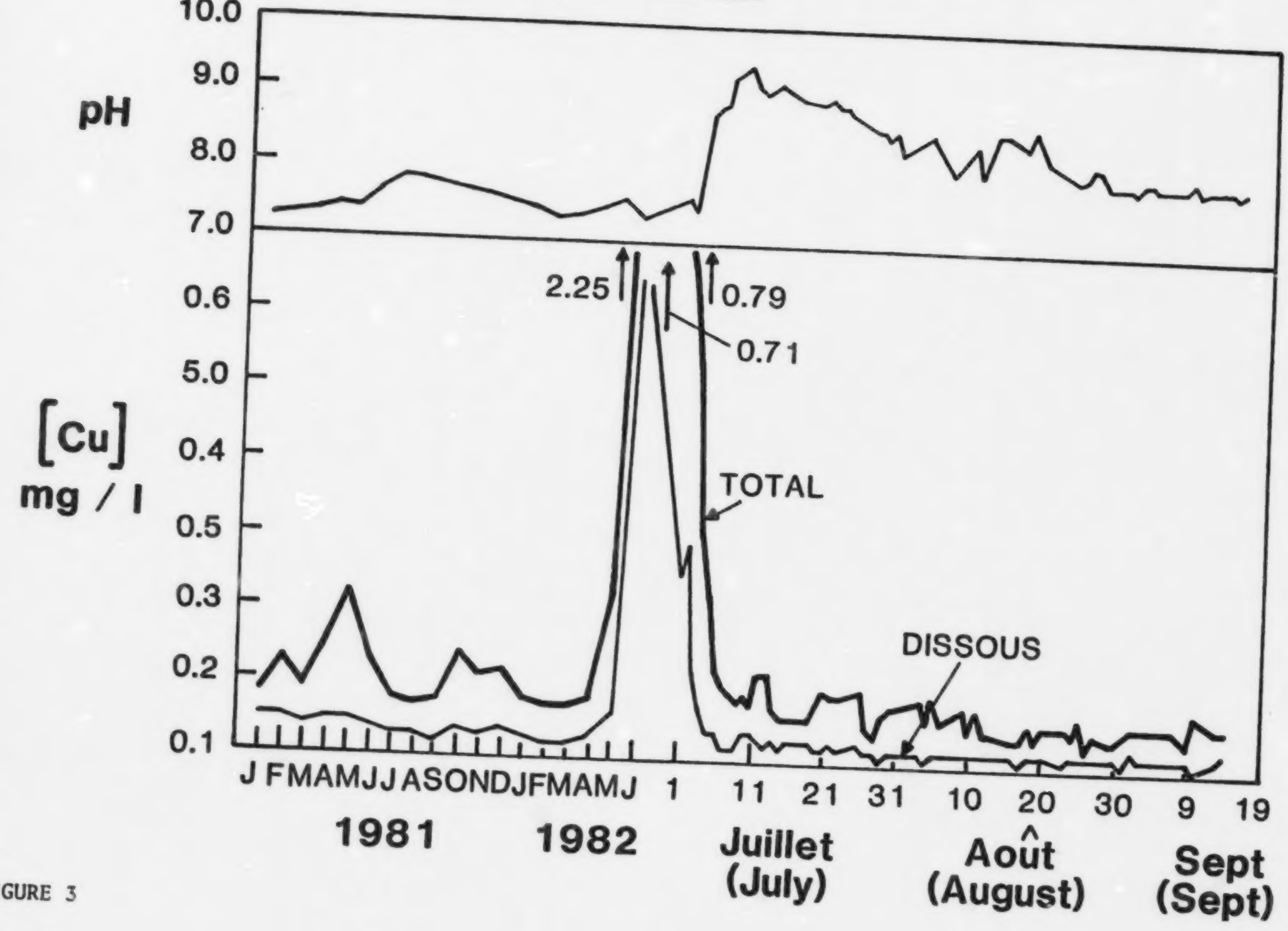

FIGURE 3

concentrations de cuivre.

Toutefois, l'effluent final n'a fait que refléter l'atténuation qui s'est chimiquement passée dans le bassin de récupération situé en amont.

3.2.2 Le cuivre total et dissous du bassin de récupération

Suite au chaulage intensif de l'eau du bassin de récupération et au maintien d'un pH supérieur à 8, le cuivre dissous a présenté une concentration généralement inférieure à 0,05 mg/l.

L'eau de surface a offert une concentration plus faible du métal dissous que l'eau en profondeur.

De même, le cuivre total a présenté une tendance similaire en affichant une concentration plus forte en eau profonde qu'en surface. La figure 4 met en relation les concentrations en cuivre total et dissous pour l'eau de surface et de fond du bassin de récupération.

Cette figure présente aussi au lecteur une augmentation dans la concentration de cuivre total dans l'eau profonde vers la fin août 1982. Nous sommes d'avis que cette hausse de concentration a été causée par un mouvement de la thermocline qui, à cette période de l'année, tend à se résorbée au profit d'une isothermie dans la colonne d'eau. Dès lors il y a brassage des eaux et, tel qu'illustré à la figure 5, rapprochement des valeurs de pH.

D'ailleurs au début septembre 1982, suite à la sédimentation des particules qui avaient été remises en suspension en eau profonde, les valeurs de cuivre total pour l'eau de surface et de fond se chevauchent.

Vers la mi-septembre 1982, l'ajout de chaux hydratée dans le bassin de récupération a cessé et, lentement, la concentration des métaux et les valeurs de pH ont retourné à leur condition normale de bonne qualité.

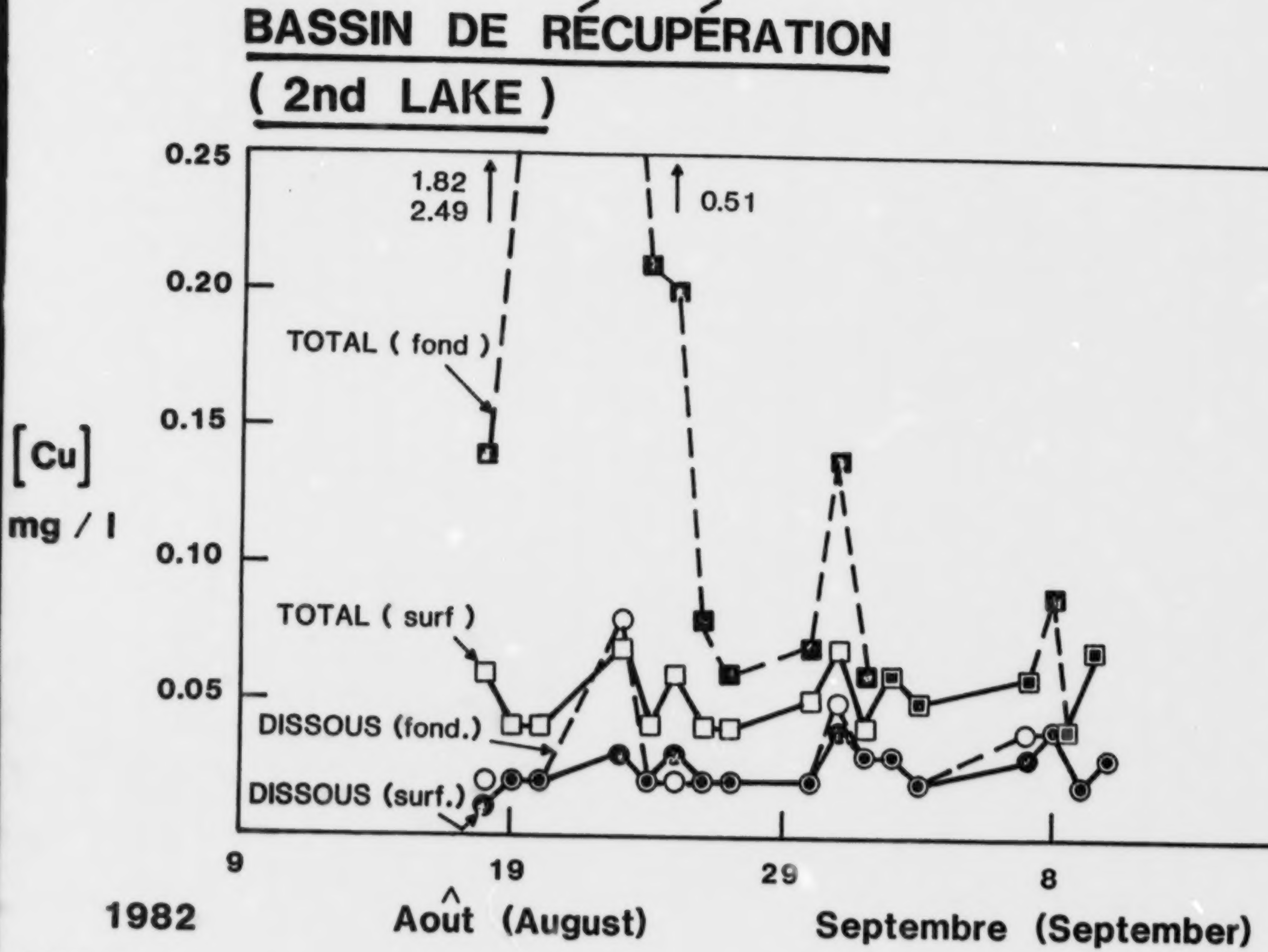
BASSIN DE RÉCUPÉRATION
(2nd LAKE)
[Cu]
mg / l
0.25
0.20
0.15
0.10
0.05
1.82
2.49
0.51
TOTAL (fond)
TOTAL (surf)
DISSOUS (fond.)
DISSOUS (surf.)
9
19
29
8
18
1982
Août (August)
Septembre (September)

FIGURE 4

BASSIN DE RÉCUPÉRATION
(2nd LAKE)

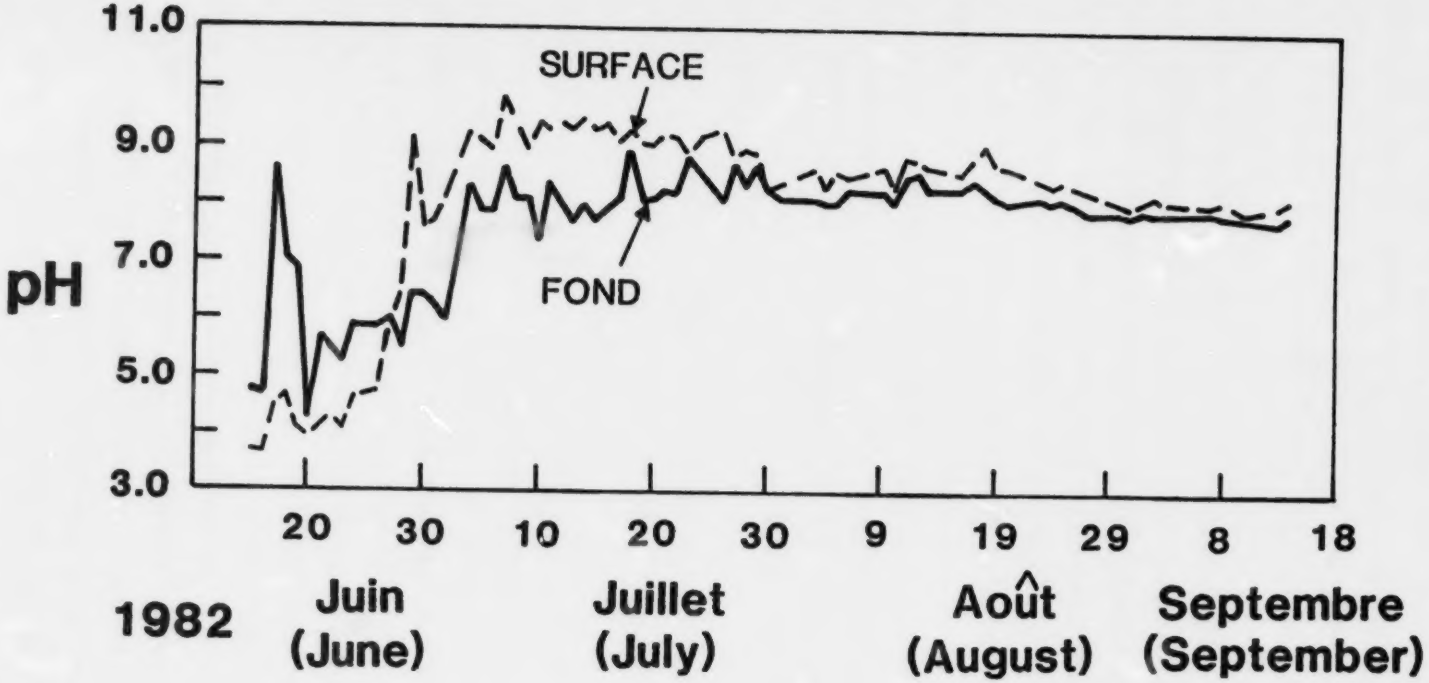

FIGURE 5

4.0 IMPACT DU DÉVERSEMENT SUR LA FAUNE AQUATIQUE DE LA RIVIÈRE YORK

La rivière York originant de l'apport de deux tributaires, les branches Sud et Nord, est considérée comme l'une des meilleures rivière à saumons de l'Atlantique (Salmo salar) de la Péninsule gaspésienne.

Pour le lecteur qui n'est pas familier avec le cycle vital du saumon de l'Atlantique disons qu'il lui faut environ cinq années de vie pour devenir adulte. Les trois premières années sont vécues en eau douce tandis que les deux années subséquentes sont passées en mer. Ce n'est qu'après ce premier laps de temps initial de cinq ans que le saumon viendra se reproduire en eau douce, généralement, dans sa rivière natale. Après le frai, il retournera en mer et s'il n'est pas capturé ou proie, il reviendra frayer l'année suivante. Le saumon de l'Atlantique débute généralement sa montaison au début juin et fraye vers la mi-octobre. D'autre part, les saumons juvéniles agés de trois ans et plus migrent en mer pour la première fois dans le mois de mai, soit après la débacle.

Afin de cerner l'étendue des impacts, entre autres, sur le cycle complexe du saumon, une étude biologique a été initiée dès juillet 1982 sur la rivière York.

4.1 Conditions générales de la rivière

La rivière York a une longueur de plus de 100 Km. La zone d'impact biologique a été identifiée comme étant les premiers 18 Km partant de l'aval du bassin de récupération et se poursuivant dans la partie supérieure de la rivière à proprement dit.

Le lit de la branche Sud, situé immédiatement en aval du bassin de récupération, était recouvert par endroit d'un mélange de pierre à chaux et de chaux hydratée ayant réagit et formant une couverture de gypse. Ces sédiments renfermaient des concentrations élevées de manganèse et de cuivre mais aussi de zinc, de fer et d'aluminium.

En aval de la branche Sud, c'est-à-dire à la tête de la rivière York, la sédimentation des produits neutralisants était minime. Une portion des pierres formant le lit de la rivière était, tout ou plus, recouverte d'une mince couche de dépôt. Ces dépôts disparaissaient complètement bien avant la fin du secteur de 18 Km consideré comme la zone d'impact biologique.

4.2 Comportement des saumons adultes

Les saumons adultes, ou géniteurs, avaient débuté leur montaison en eau douce lorsque le déversement a eu lieu. La hausse dans la concentration des métaux lourds, due à l'eau acidulée, a provoqué un retour dans la zone de mélange eau douce-eau salée de ceux déjà en rivière. Le pH ayant été maintenu stable entre 7 et 8, ce facteur physique a été exclus comme cause directe du comportement d'évitement.

Suite à l'ajout de neutralisants, les métaux dissous du bassin de récupération se sont précipités et la qualité de l'eau était redevenue normale vers le début juillet 1982. Dès lors une deuxième remontée des saumons adultes avaient commencé lorsque vers la fin juillet de fortes pluies tombèrent. Ces précipitations eurent pour effet de gonfler le débit de la rivière tout en lessivant les sédiments et les dépôts gypseux du lit. La remise en suspension de ces matériaux, couplés à une libération des métaux qu'ils renfermaient, fit rebroussé chemin une autre fois aux saumons. Il est à noter que le court laps de temps entre le contrôle des pH du bassin de récupération et l'avènement des pluies n'a pas permis de procéder à l'enlèvement des sédiments et dépôts gypseux alors présent sur le lit du tributaire de la rivière.

Nous sommes d'avis que le comportement d'évitement observé chez les saumons a été provoqué par plusieurs facteurs difficilement dissociables. Parmi ces facteurs notons l'ensemble des métaux lourds tant sous forme dissoute que solide et l'emploi massif de produits neutralisants. Nous croyons que ces facteurs ont masqué l'identité des caractères physico-chimiques normaux de l'eau de la rivière York. Toutefois, à son embouchure, l'eau de la rivière possédait sans doute suffisamment d'identité pour faire patienter les saumons dont l'imprégnation leur dictait que c'était la bonne rivière. Dans la même veine, l'identité de la rivière se perdait à mesure que les concentrations augmentaient en amont.

Toutefois le débit élevé de la rivière a été très efficace pour le nettoyage de son lit, probablement même beaucoup plus qu'un nettoyage manuel.

Ce n'est qu'après ces pluies que les saumons adultes ont procedé à la montaison vers le début août 1982. A la fin du même mois, environ 900 saumons géniteurs étaient dénombrés dans la rivière York ce qui constituait, somme toute, un nombre normal et suffisant pour la reproduction naturelle.

4.3 Impacts sur les saumons juvéniles

Les saumonneaux agées de trois ans ou plus n'ont subi aucun préjudice attribuable au déversement d'acide étant donné que leur migration en mer était déjà complétée depuis la fin mai.

Toutefois, chez les alevins et les saumons juvéniles agés de 1 et 2 ans un taux de mortalité élevé a été enregistré dans la zone d'impact. En terme de saumons adultes, l'impact majeur sera en 1985 et se traduira par une baisse potentielle d'environ 150 géniteurs. Concernant les années 1986 - 1987, l'impact sera de moindre importance dû, entre autres, à une meillure chance de survie des alevins et des saumons juvéniles agés de un an à cette époque. Cette meilleure chance de survie est anticipée à cause d'une compétition moins forte à l'intérieur des groupes d'âge. D'autre part, une recolonisation de saumons juvéniles provenant des tributaires de la rivière York était observée dans la zone d'impact en été 1983. Cette recolonisation indique premièrement que la qualité de l'eau est bonne et que, deuxièmement, la nourriture, sous forme de benthos, est en quantité suffisante.

4.4 Impacts sur la faune benthique

La faune benthique, largement constituée de larves d'insectes, est la nourriture de base des saumons juvéniles. Pour leur part, les saumons adultes ne se nourissent généralement pas, ou peu, durant leurs séjour en eau douce pour le frai.

Le benthos dont les principaux représentants dans la rivière York sont des larves d'éphéméroptères, de trichoptères et de chironomides devient donc essentiel pour la survie des saumons juvéniles.

La zone d'impact la plus sévère sur le benthos a été observée dans la branche Sud, ce qui représente environ 1% du total des habitats de la rivière. Puisque ces invertebrés vivent attachés aux roches ou entre les interstices de celles-ci, le recouvrement, par endroit, du lit de la rivière par des dépôts gypseux a éliminé une bonne partie de cette faune.

Toutefois, à la tête même de la rivière York, soit en aval de la jonction des branches Sud et Nord, une bonne récupération était observée dès la fin août 1982. Cette section dans la zone d'impact biologique a donc été qualifiée de "qualité intermédiaire". Plus en aval, la faune benthique était diverisifée et abondante, en somme, normale pour la rivière.

Suite au lessivage des sédiments en juillet 1982, et à la recolonisation partielle de la fin août 1982, nous pouvons anticiper une récupération quasi-total en été 1983. D'ailleurs, la présence de saumons juvéniles dans la branche Sud en été 1983 laisse présager une bonne récupération de la faune benthique.

5.0 ÉTUDE HYDROGÉOLOGIQUE DU SITE DU DÉVERSEMENT

En parallèle à l'étude biologique sur la rivière York, une étude hydrogéologique du sous-sol environnant le lieu de déversement était initiée en juillet 1982.

Le patron de forage fut consitué de sept emplacements distribués entre l'aire de chargement des camions citernes et le ruisseau Porphyre ou se jette l'effluent de l'usine d'épuration municipale. Pour le bénifice du lecteur, la figure 6 schématise l'allure du site de même que l'emplacement des trous de

LIEU DU DÉVERSEMENT-HYDROGÉOLOGIE
(SPILL AREA - HYDROGEOLOGY)

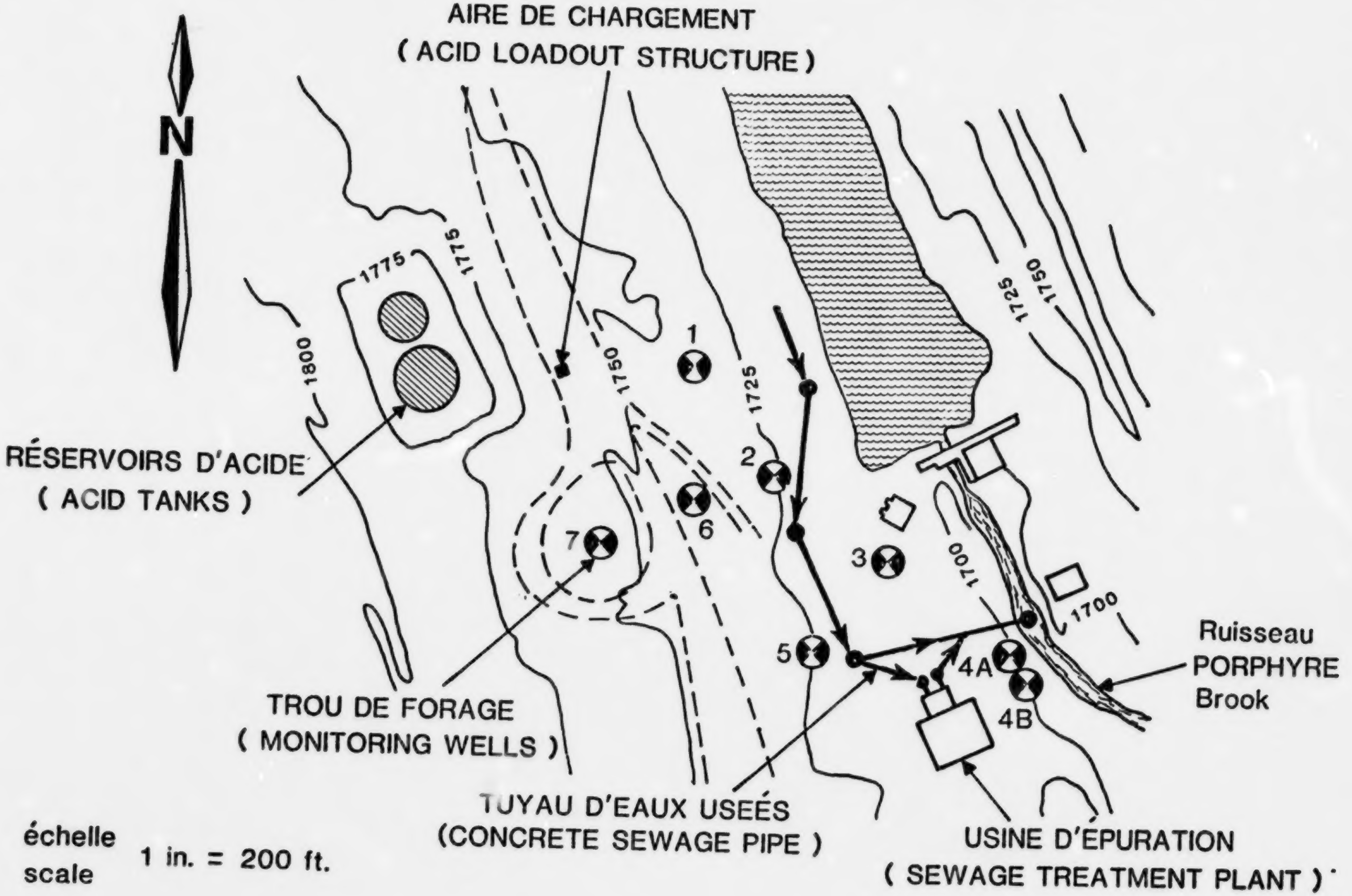
AIRE DE CHARGEMENT
(ACID LOADOUT STRUCTURE)
N
1775
1775
1800
1750
1725
1725
1750
1700
1700
1
2
3
4A
4B
5
6
7
RÉSERVOIRS D'ACIDE
(ACID TANKS)
TROU DE FORAGE
(MONITORING WELLS)
TUYAU D'EAUX USEÉS
(CONCRETE SEWAGE PIPE)
USINE D'ÉPURATION
(SEWAGE TREATMENT PLANT)
Ruisseau
PORPHYRE
Brook
échelle
scale
1 in. = 200 ft.

FIGURE 6

forage.

5.1 Sommaire géologique du sous-sol

Le ruisseau Porphyre qui est tributaire de la branche Sud de la rivière York est situé au fond d'une vallée formée suite au passage des glaciers. Le lit du ruisseau est constitué de dépôts alluviaux sous lesquels du till glaciaire va jusqu'au roc. Tant qu'au roc, il est composé d'un silt calcaireux gris foncé, typique de la formation de Grande Grève. Cette formation, née en conjonction avec d'autres strates de le l'ère Dévonienne moyenne et inférieure, inclus de la pierre à chaux, du schiste argileux et du grès. Les diverses formations de roc révèlent, en général, plusieurs failles dans la région. Quoique la zone minéralisé exploitée par Mines Gaspé soit à proximité, le lieu du déversement n'en fait pas partie.

La formation de Grande Grève a été rencontrée à une profondeur d'environ 11 mètres lors du forage. Suite à l'analyse des carottes de forage, les horizons du soubassement (bedrock) de l'aire du déversement ont une inclinaison d'environ 45° vers le Nord, Nord-Ouest. Ce roc contient en moyenne 66% de silice, 20% de carbonate de calcium, 5% de carbonate de magnésium, 5% d'oxyde de fer et 4% d'autres constituants. D'autre part, il a été établi, à l'aide d'un double essai "packer", que le coefficient secondaire de perméabilité du roc est de l'ordre de 3×10^{-5} à 2×10^{-13} cm/sec pour les 4,5 mètres supérieurs de roc et qu'il est générallement moins de 3×10^{-5} cm/sec pour la partie inférieure.

Concernant le sol situé au-dessus du roc, il est constitué de till glaciaire composé de sables limoneux, de graviers et de moellons. Sa perméabilité va de faible à intermédiaire. Il est à noter que les premiers mètres de cette couche de sol ont été remaniés plusieurs fois à cause des nombreuses constructions effectuées dans les environs.

5.2 Tracé souterrain de la fuite d'acide

La fuite d'acide a emprunté un trajet originant du sous-sol de l'aire de chargement des camions citernes dont les fondations bétonnées sont à une élevation de 1 742 comparativement à la surface du roc qui, à cet endroit, à une élévation de 1 740. Il semble, selon les évidences des résultats, que l'acide a rejoint le roc peu après avoir fuit.

De là, et considérant que peu ou pas d'acide a été retrouvé dans les puits de forage 1, 2 et 7 et que, par contre, la concentration d'acide était forte au puit de forage 6, l'acide a migré selon une orientation Sud-Est en provenance de l'aire de chargement.

Ce trajet est toutefois étonnant car selon les courbes de niveaux l'acide aurait dû se diriger vers l'Est. Toutefois plusieurs facteurs ont pu causer un écoulement préferentiel en direction du Sud-Est. Parmi ces facteurs notons la présence d'une nappe d'eau souterraine ayant pu créer une barrière hydraulique à l'acide et la présence possible d'une ligne de discontinuité à haute perméabilité dans le roc ayant une orientation Sud-Est. D'autres facteurs tels les nombreuses excavations qui ont eu lieu sur le site ou encore la mise en évidence d'une ligne de transition entre l'écoulement de l'eau souterraine du till glaciaire et du roc peuvent avoir contribués à orienter le trajet de l'acide. Quoique cette ligne de transition coïncide avec le trajet souterrain de l'acide, il est très difficile d'identifier lequel des facteurs, mentionnés précédemment, a été prépondérant. Il semble plutôt que ce soit une combinaison de ces facteurs qui a influencé le trajet du panache d'acide.

Ensuite, l'acide s'est infiltré dans la canalisation des eaux usées. Lorsque infiltré, l'acide a simplement suivi le parcours des eaux à épurer pour, finalement, se déverser dans le ruisseau Porphyre par le biais de l'effluent de l'usine municipale.

Concernant les puits de forage 3, 4 et 5, aucune présence évidente d'acide n'a été observée. Enfin, en amont de la sortie de l'effluent de l'usine d'épuration, le ruisseau Porphyre offrait un pH normal.

5.3 Mesures d'atténuations

Malgré l'ampleur du déversement, peu d'acide est demeuré dans le sol. En effet, le chemin préférentiel qu'à emprunté le panache a permis de drainer la quasi-totalité de la fuite dans le ruisseau adjacent à l'usine d'épuration.

Comme nous l'avons déjà mentionné à la section 2 de la présente publication, diverses mesures de mitigations furent mises en place pour limiter les effets environnementaux. Toutefois, lorsque le pH de l'effluent de l'usine d'épuration s'est rétabli, il était sujet à redevenir acide lorsqu'il pleuvait.

Afin de maintenir un pH 7, pour permettre le bon fonctionnement de l'usine, l'ajout de neutralisant directement dans la canalisation menant l'usine d'épuration, a du être effectué par temps pluvieux. Pour ce faire de la soude caustique ($NaOH$, 20%) alimentait par gravité la canalisation par le biais d'un trou d'homme. Ce neutralisant liquide était entreposé dans un camion citerne stationné en permanence près du point de déversement.

La figure 7 présente au lecteur la relation qui s'est établi entre les précipitations et la baisse de pH à l'effluent municipal. Ainsi en juillet 1982, alors que aucun neutralisant n'était ajouté dans la canalisation, le pH devenait rapidement acidique sous l'influence de la pluie. Les précipitations, en percolant dans le sol, agissaient en rehaussant le niveau de la nappe phréatique et permettaient à l'acide de s'infiltrer dans la canalisation.

Vers la mi-août 1982, le système de neutralisation par soude caustique fut mis en place et opéra, au besoin, de l'automne 1982 au printemps 1983. Un total approximatif d'environ 40 tonnes de $NaOH$ (20%) a été utilisé durant cette période. Concurremment à la purge naturelle de l'acide, une neutralisation dû aux carbonates de calcium contenu dans le sol s'effectuait.

PRÉCIPITATIONS vs pH EFFLUENT MUNICIPAL
(SEWAGE EFFLUENT)

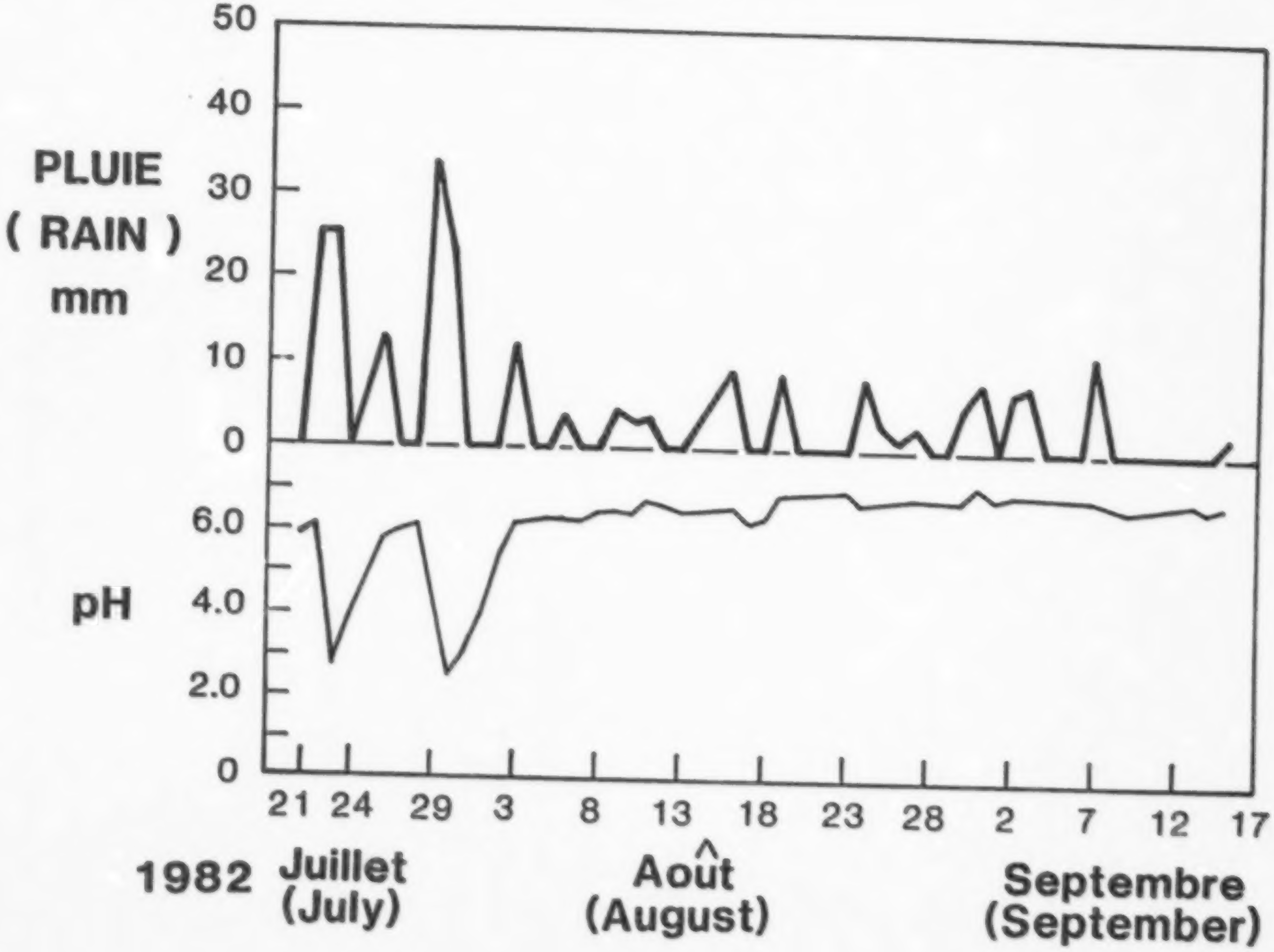

FIGURE 7

Un suivit de la concentration d'acide présente dans l'eau du puit de forage 6 a montré un affaiblissement progressif de l'agent agresseur. Ainsi de août 1982 à avril 1983, l'eau du puit de forage 6 a eu une concentration d'acide sulfurique décroissante et respectivement de 0,261% et 0,039%. En été 1983, aucun ajout de neutralisation n'a été nécessaire. Le pH de l'effluent municipal demeurait normal et stable même lorsqu'il pleuvait.

6.0 MESURES PRÉVENTIVES

Suite à cette expérience, divers travaux ont été exécutés afin de prévenir et détecter d'éventuelles fuites d'acide.

Dans un premier volet, le tuyauterie acheminant l'acide des réservoirs d'entreposage à l'aire de chargement des camions citernes a été déterée puis installée en surface. Cet ouvrage permet une inspection visuelle rapide et efficace de l'état du système et, le cas échéant, de localiser rapidement une fuite. Dans la même veine, un double système de vannes, électriques et manuelles, a été installé tant à la sortie des réservoirs qu'à l'entrée de l'aire de chargement. Auparavant, seul un système de vannes manuelles était utilisé.

Dans un deuxième volet, l'endiguement autour des réservoirs de rétention a été recouvert d'une membrane imperméable. Advenant le bris accidentel d'un réservoir, son contenu sera confiné à l'intérieur de l'endiguement.

Dans un troisème volet, la tuyauterie et la base des réservoirs ont été munies de fils électriques dont la gaine protectrice fond au contact de l'acide et provoque un court circuit qui déclenche une alarme. Ce système est aussi couplé à une jauge électrique qui indique les niveaux d'acide présents dans les réservoirs d'entreposage. Toutefois, une lecture manuelle des niveaux est toujours effectuée, au moins une fois la semaine, ce qui permet, du même coup, une inspection visuelle des lieux.

7.0 CONCLUSION

Ce déversement d'acide, à la tête d'une rivière à saumons, a été unique au monde. De même en est-il de l'expérience acquise pour contrer les effets de l'agent agresseur. Un esprit d'équipe sans précédent a été la clé du succès et les auteurs tiennent à remercier le personnel de Mines Gaspé pour leur persévérance de même que pour la précision et la rapidité du travail exécuté.

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A SPILL HAZARD RANKING SYSTEM FOR CHEMICALS

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INTRODUCTION

Public concern about the transport of chemicals has been heightened recently by two incidents which have received considerable investigation and publicity.

On November 10, 1979 a CP train derailed in Mississauga (near Toronto) as a result of a hot box on a toluene tank car. Some 23 other cars were derailed discharging several cargoes including chlorine, styrene and propane, resulting in a fire and eventually evacuation of over 200,000 people (Grange, 1981). On March 10, 1980 a CN train derailed about 2 km west of MacGregor, Manitoba. Twenty-one cars were derailed, twelve of which contained vinyl chloride monomer, two of which leaked (CTC, 1980).

Fortunately, in neither case was there loss of life. If either accident has occurred under slightly different circumstances there could have been a massive death toll on the scale of the 1917 Halifax Harbour tragedy.

Accidents such as these generate inquiries into cause and inevitably recommendations ensue which seek to avoid recurrence. Of particular interest is the set of recommendations which arose from the enquiry conducted by Hon. Mr. Justice Samuel G.M. Grange into the Mississauga incident (Grange, 1981). A key point of the recommendations is that trains "transporting dangerous goods of any kind" should be equipped with roller bearings, double shelf couplers and in many cases, head shields, thermal protection, bottom fitting protection, and should not exceed a speed of 25 miles per hour. The Canadian Transport Commission (CTC) issued an order to the railways to show cause why these recommendations (and others) should not have effect. The responses predictably claimed that implementation of the recommendations would incur a severe economic penalty, result in interruption of service to customers, higher freight rates, could not be implemented as rapidly as was suggested due to supply and conversion problems and in any event would not necessarily improve the general goal of increased rail safety. A public hearing resulted to expose the issue in its entirety and the findings were published (CTC, 1981).

It is clear that the issue is very much more comlex than is generally appreciated. Intuitively, it seems reasonable that dangerous goods should receive special treatment, as indeed is practised by the transportation industry. But the public perception is clearly that present practices are not adequate and extra preventative measures are justified as, for example, suggested by Grange. Protestations of economic penalties, complexity of the issues, etc., etc., tend to fall on unsympathetic ears when human safety is seen to be threatened.

Given the clash of two imperatives - human safety at any price - and continued economic operation of the transportation industry, it is apparent that some middle course should be sought to improve the safety of dangerous commodity transportation, but the measures should not cripple the industry. Of the options which are available, one of the most attractive is to select from the long list of dangerous goods, those which are "highly dangerous" such that they could cause significant public mortality or injury. Perhaps a small group of goods can be identified for which extraordinary measures may be justified.

For example, they could be conveyed only in vehicles of high standard which are subjected to more rigorous inspection. They could be specially placarded and personnel alerted and trained to their unusually high hazard potential for disaster. They could be transported only at certain times and on selected routes.

The smaller this group of highly dangerous chemicals, the smaller will be the economic and technical problems and the more likely will be the ready acceptance by industry. In this paper, some principles are examined which could govern the selection of candidates for this group. In essence, we dispute Justice Grange's contention that the regulations should apply to dangerous goods "of any kind". Perhaps a gradation in dangerousness is appropriate.

SELECTION OF HIGHLY DANGEROUS CHEMICALS

The CTC "Red Book" lists some 5000 dangerous commodities and specifies the treatment which they should be accorded. Other compilations are available, for example, the "Emergency Response Guide for Dangerous Goods" (Transport Canada, 1979). This Guide classifies goods into four categories for evacuation purposes.

Commodities are usually dangerous because of their toxicity, or tendency to ignite or explode or react rapidly (corrode) such that they may damage other containers as well as inflict injury to those who may be exposed. Since it is the public which is of primary concern, it is logical to concentrate on those commodities which have the potential to exert injurious effects at a distance. It is recognized that for example in the case of rail accidents, the public may be only metres from trains at crossings and stations but the primary concern is that a large number of people could be affected, possibly while they sleep, say 200 m from the tracks. Prime candidates are thus materials such as chlorine or vinyl chlorine monomer which, when spilled, could release a vapor plume or cloud which envelope a populous area resulting in a toxic effect or explosion and considerable loss of life.

Perhaps there are three initial selection criteria:

1. Quantity of material present in the shipment.
2. Potential of the material to generate a plume.
3. Hazard resulting from that plume.

To be a candidate the material must satisfy all three. This would eliminate materials such as sulphuric acid (no plume), liquid CO_2 (no real hazard), and small containers of dangerous materials. Such a categorization is necessarily subjective and thus potentially controversial. A fourth criterion which is arguable from an overall safety policy viewpoint is:

4. Total quantity transported annually.

There are some questions about the validity of (4) from the viewpoint that one car-load of rarely transported material is as hazardous as one car-load of frequently transported material (with similar properties) but the public exposure to hazard is greater when the quantity handled increases and it is perhaps appropriate to address the largest exposure problems first.

In this paper a system is devised for rating chemicals according to hazard, based on precisely defined chemical properties. It is important for regulatory purposes that the process of selection be clearly defined and defensible.

THEORETICAL ANALYSIS OF PLUME FORMATION AND DISPERSION

The approach here is to calculate the likely concentrations in a plume as a function of the spill variables in order to (i) permit an estimate to be made of concentration relative to a "toxic effect" concentration and (ii) to develop a group of variables with which to rank materials according to their hazard.

Consider a volume of material $V m^3$ of density ρ kg/m^3 spilled to cover an area $A m^2$, the average depth thus being $V/A m$. The subtance's liquid molar volume is $v m^3/mol$. The evaporation rate Q kg/s is given by

$$Q = KAPM/RT \qquad (1)$$

where K is a mass transfer coefficient m/s, P is the liquid vapour pressure (Pa), R the gas constant (Pa m^3/mol K), T is absolute temperature (K) and M is molecular weight (kg/mol). Justification is given in a paper published elsewhere in these proceedings.

Considering the simple Gaussian plume dispersion model for concentrations along the centre line and at zero vertical displacement (i.e., y and z are zero) gives (Turner, 1970).

$$C = Q/\pi U \sigma_y \sigma_z \qquad (2)$$

Here C is concentration (kg/m^3), U is wind speed (m/s), σ_y and σ_z are the horizontal (lateral) and vertical dispersion coefficients (m). Plume reflection at the ground is assumed.

If class C conditions are assumed then if x is the downwind distance the horizontal term σ_y is approximately 0.1 x and the vertical term σ_z is 0.06 x, thus

$$C = Q/(\pi\ U\ 0.006\ x^2) \qquad (3)$$

An approximation for K the mass transfer coefficient is (Mackay and Matsugu 1973)

$$K = 0.002\ U\ m/s \qquad (4)$$

Finally, if a concentration is expressed in parts per million by volume then

$$C\ (ppm) = C_T = 10^6\ C\ RT/P_A M \qquad (5)$$

where P_A is atmospheric pressure (101000 Pa).

Equations 1 to 5 can be solved to relate C_T to x yielding

$$C_T = 1.05\ PA/x^2 \qquad \text{The constant has unity of (ppm/Pa).} \qquad (6)$$

Interestingly, the wind velocity cancels because although it increases the evaporation rate it also reduces the concentration by dilution. Equation 6 suggests (as is intuitively obvious) that concentration is linearly related to vapour pressure and spill area and inversely proportional to the square of the distance. If the distance is calculated correspondingly to the occurrence of some limiting desirable concentration C_T (such as a flammability limit or toxic concentration) then

$$x = 1.02 \sqrt{PA/C_T} \quad \text{The constant has units of } (\text{ppm/Pa})^{1/2}. \quad (7)$$

This suggests ranking chemicals according to an index of vapour pressure to an "effect concentration" but a better indication of relative hazard magnitude may be obtained by taking the square root. This approach is similar to that suggested recently by Pitt (1982) who has used ratio of concentration of saturated vapour to Threshold Limit Value (TLV) as a "Vapour Hazard Index".

There is a problem in predicting P, the material vapour pressure. For compressed materials such as propane which have boiling points below ambient temperature, the maximum value will be 1 atm, i.e., the liquid will flash cool to close to its boiling point. In practice the pool temperature is affected by evaporation rate, heat transfer rate from the substrate and solar insolation. As an approximation it is suggested that the vapour pressure at 25°C be used except if this exceeds 1 atm, at which 1 atm (101325 Pa) is used.

RESULTS AND DISCUSSION

Equation 7 is the basis for ranking chemicals for their hazard in the event of a spill. Factors which are influenced by the spill situation and are not a function of the chemical are all combined in the constant. The area term is largely a function of the amount of chemical spilled. However, this is a function of the situation and is not included in the criterion.

The vapor pressure used is that for the specific chemical of interest and must not exceed 1 atm as mentioned earlier. For ranking purposes the vapor pressures were determined at a temperature of 25°C.

The major problem is determining which value to use for the concentration. For chemicals in which the concern is about the toxicity to humans there are many choices. The hazardous concentration most widely available is the threshold limit value (TLV). The TLV is the occupational exposure which, it is believed, over a 40 hour work week will not have chronic health effects on the employee. In the chemical spill situation the concern is usually with a very high exposure over a short period of time.

A second concentration which is not as widely available is the short term exposure limit (STEL). This is the concentration the worker can be exposed to for only short periods of time. However, the worker can be exposed to this concentration several times a day; it is still a chronic exposure criterion.

A third concentration is the ceiling concentration. It is an absolute maximum exposure and characterizes the acute affects of the chemicals. The ceiling concentration is more applicable to the chemical spill situation but data for ceiling concentrations are not so generally available.

For illustration purposes we have compiled in Table 1 selected data on vapour pressures at 25°C and TLV concentrations and calculated the index as the square root of the ratio. When the vapour pressure exceeds atmospheric presure, 100000 Pa was used. These index values (e.g., 35 for benzene) represent approximately the minimum downwind distance that personnel should approach a 1 m^2 spill, if they are to experience a maximum TLV concentration, under the prescribed weather conditions.

Table 1
Toxicity Index for Various Chemicals

Compound	Vapour Pressure (kPa)	TLV (ppm by vol.)	Toxicity Index (m)
Phosgene	190*	0.1	1000
Chlorine	870*	1	316
Vinyl chloride	395*	5	140
Ethylene oxide	200*	10	100
Cyanogen gas	570*	10	100
Anhydrous ammonia	990*	25	63
Carbon tetrachloride	14.9	5	55
Benzene	12.3	10	35
Acrylonitrile	15	20	27
n-hexane	20.2	500	6.3
Toluene	3.79	100	6.2
Styrene	0.54	50	3.3
Phenol	0.05 (20°C)	5	3.2
Ethylene glycol	0.01	100	0.3

* 101000 Pa used in index.

Table 2 gives the fire hazard ranking in which the lower flammability limit (which is normally expressed as percent by volume) is expressed as part per million (i.e., a factor of 10^4 greater). Again the index represents an approximate safe approach distance on the downwind side for a 1 m^2 spill.

Table 2
Flammability Index for Various Chemicals

Compound	Vapour Pressure (kPa)	LFL (ppm by vol. $\times 10^{-4}$)	Flammability Index (m)
Butadiene	270*	2.0	2.3
Propane	1000*	2.2	2.1
Pentane	68.4	1.5	2.1
Vinyl chloride	395*	3.6	1.7
Ethylene oxide	200*	3.6	1.7
Benzene	12.3	1.3	0.97
Ammonia	990*	15	0.82
Acrylonitrile	15	3.0	0.71
Toluene	3.79	1.2	0.6
Styrene	0.54	1.1	0.22
Phenol	0.05	1.8	0.05
Ethylene glycol	0.01	3.2	0.02

* 101000 Pa used in index.

The principal merit of this approach is that it generates a simple ranking scheme based on widely accepted data. A substance such as ammonia ranks relatively high despite the common perception that it is fairly non hazardous, being widely used in agriculture. There are several weaknesses which deserve emphasis.

The use of TLV is not desirable since it is established for quite different purposes. Even a multiple of TLV is suspect. More short term exposure concentrations should be established. It is also desirable to gather data on actual downwind concentrations for selected substances to determine the inherent validity (or lack of it) of the evaporation-dispersion equations. The concentrations temperature dependence and dependence on ground conditions such as snow cover should be investigated. Finally, there is a need to integrate information of this type and make it more readily and rapidly available to those who respond to chemical spill situations in order that the public and the response personnel be better protected.

CONCLUSIONS

The theoretical basis for ranking the hazards of chemical spills has been developed. The simple square root of the raio of a chemical's vapour pressure to its toxic or flammable concentration given a measure of the risk for a particular chemical. This ratio is related to the minimum approach distance. The rating eliminates factors that change from spill to spill (i.e., wind speed, amount of chemical) but incorporates the dispersion, volatility and toxicity of the chemical in a fairly rigorous manner.

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SUPERFUND HAZARDOUS SUBSTANCE NOTIFICATION REQUIREMENTS AND REPORTABLE QUANTITY ADJUSTMENTS

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BACKGROUND

This paper was prepared to provide participants of the "Technical Seminar on Chemical Spills," with an overview of the U. S. Environmental Protection Agency's most recent efforts to regulate hazardous substance release notifications pursuant to existing statutory requirements. The principal statutory requirements governing hazardous substance release reporting and response are the Comprehensive, Environmental Response, Compensation, and Liability Act (CERCLA) and the Clean Water Act (CWA), also known as the Federal Water Pollution Control Act (FWPCA). This paper discusses these authorities to control and regulate the release of designated hazardous substances and the basic methodology used to adjust reportable quantities (RQ's) of designated hazardous substances.

The most comprehensive statutory authority is vested in CERCLA, which designates approximately 700 hazardous substances. Section 102(b) of CERCLA established an RQ of one pound for approximately 400 substances which do not have RQs assigned previously from the CWA. These RQs shall remain at one pound unless and until superceded by regulation under CERCLA section 102.

The U. S. Environmental Protection Agency (EPA) has developed a scientific methodology called Selective Criteria Processing (SCP) for adjusting RQs for application to releases into all media (land, air, and water). The SCP utilizes six primary criteria in the RQ adjustments: aquatic toxicity, mammalian toxicity, ignitability, reactivity, carcinogenicity, and chronic toxicity. This paper discusses the application of the SCP and explains the use of RQ's in the Superfund notification program.

Clean Water Act

Under the authority of the Federal Water Pollution Control Act (FWPCA) section 311(b)(4), the Environmental Protection Agency (EPA) promulgated regulations establishing a federal notification system for discharges of hazardous substances into navigable waters. 40 CFR Part 116 designates 297 substances as hazardous; 40 CFR Part 117 establishes reportable quantities (RQs) for these substances. When a hazardous substance is discharged into navigable waters in a reportable quantity, the discharger is required to notify the appropriate Federal official (the On-Scene Coordinator). Both the EPA and the United States Coast Guard (USCG) are the responding Agencies to these notifications, and provide On-Scene-Coordinators (OSC's) for this purpose. EPA handles discharges to inland waters, whereas the USCG has response jurisdiction to discharges in the coastal waters. The National Response Center (NRC), which is operated and staffed by the USCG, is the designated source to receive all calls directly; and to forward them to the OSC in the shortest possible time frame.

CERCLA

The Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA or Superfund) provides for liability, compensation, cleanup, and emergency response for hazardous substances released into the environment and the cleanup of inactive hazardous waste sites. Although much more comprehensive in nature, CERCLA adopts several of the Clean Water Act (CWA) section 311 regulatory provisions into its statutory and regulatory framework, as will be seen below. The notification mechanism utilized under the CWA is adopted within the CERCLA statutory language. The NRC is required to review the release notifications and forward them to the OSC in the shortest possible time frame.

CERCLA section 101(14) statutorily designates an initial list of 696 hazardous substances. This list includes substances designated under certain provisions of other environmental statutes:

- Chemicals listed under Section 311 of the CWA;
- Hazardous wastes having the characteristics identified under or listed pursuant to section 3001 of the Resource Conservation and Recovery Act (RCRA);
- Toxics listed under section 307(a) of the CWA;
- Hazardous air pollutants listed under section 112 of the Clean Air Act (CAA);
- Imminently hazardous substances under section 7 of the Toxic Substances Control Act; and
- Any substances designated by the Administrator as hazardous under section 102 of CERCLA.

Section 102(a) authorizes the Administrator to promulgate regulations to designate as hazardous substances other elements, compounds, mixtures, solutions, and substances that may present substantial danger to public health or welfare or the environment when released into the environment. Furthermore, section 102(a) provides the authority to set reportable quantities for all those hazardous substances listed pursuant to section 101(14), as well as those designated under 102(a). Unless and until such time that the Administrator sets new reportable quantities for these substances, a statutory RQ of one pound has been established pursuant to section 102(b) for all hazardous substances except those with RQs already established under the CWA section 311.

CERCLA Notification Requirements

As soon as a responsible party has knowledge of the release of a hazardous substance in an amount greater than or equal to its RQ, notification must be given immediately to the National Response Center (NRC) pursuant to CERCLA section 103(a). Section 101(22) defines release as "any spilling, leaking, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment." Certain releases, however, are excluded from the section 103(a) notification requirements. These exclusions include: some releases which result in exposures to persons solely within the work place; some emissions from engine exhaust; releases of source, byproduct, or special nuclear material from a nuclear incident, as defined in the Atomic Energy Act of 1954, and if the release is subject to financial protection requirements established under the Price Anderson Act; and the normal application of pesticides. Federally permitted releases, as defined under section 101(10) of the Act, are also exempt from CERCLA section 103(a),(b), and (f) notification requirements.

Continuous Releases

Section 103(f)(2) provides for a partial exemption to the section 103(a) and (b) notification requirements. Releases may be exempt if they are "continuous", "stable in quantity and rate", and notification has been given under sections 103(a) and (b) "for a period sufficient to establish the continuity, quantity, and regularity" of the release or under section 103(c). Notifications of continuous releases must be given "annually, or at such a time as there is any statistically significant increase" in the quantity of the hazardous substance being released. Because the terms in this section of the Act are undefined, the Agency cannot implement a continuous release notification system until a policy or regulation has been developed. The Agency is presently reviewing comments on how best to handle continuous releases, among other issues presented in its May 25, 1983, Federal Register Notice.

Mechanics of Notification

Once the RQ of a CERCLA hazardous substance has been released into the environment, notification must be made immediately by telephone to the NRC which is manned by the United States Coast Guard (USCG). The toll-free telephone number of the NRC ((800) 424-8802) is accessible from all 50 states. Penalties, including criminal sanctions, have been established under section 103(b) for persons in charge of vessels or facilities who fail to report releases of hazardous substances which equal or exceed the reportable quantity. Any person who, as soon as he has knowledge of a reportable release, fails to report such a release is subject to criminal liabilities for failure to notify, a $10,000 fine and/or up to one year in prison.

Reportable Quantity Adjustments

On May 25, 1983, the Agency published in the Federal Register a Notice of Proposed Rulemaking (NPRM) on Superfund Notification Requirements and Reportable Quantity Adjustments. This proposal put forth RQ adjustments for approximately 60 percent of the hazardous substances listed under section 101(14) of CERCLA. The remaining 40 percent of the list will be the subject of a separate and upcoming rulemaking effort.

Because Congress established an RQ of one pound for approximately 400 substances which did not have RQs previously assigned from the CWA, the Agency embarked upon the above mentioned rulemaking in order to: (1) provide a sensible RQ methodology for releases to all environmental media; (2) provide regulatory certainty to the regulated community and emergency response personnel; (3) focus Federal resources on the most serious releases; and (4) present, for the first time, the definitive list of statutory hazardous substances designated under CERCLA.

What is an RQ?

The reportable quantity is that amount of a particular CERCLA hazardous substance which, when released into the environment, requires an immediate notification to the NRC. The RQ does not equate to "actual" harm; it relates to "potential" harm. It is merely a trigger for notification. Only after a Federal OSC has assessed a release situation will a determination be made whether or not a Federal field response is necessary. In a great majority of cases, the releaser or a state or local group (e.g., state agency, municipal fire department, state highway patrol) will adequately handle the cleanup of the hazardous substance release, and no Federal involvement is necessary.

Reportable Quantity Methodology

Congress gave the Agency wide discretion in adjusting the RQs for CERCLA hazardous substances. In fact, the legislative history states that "administrative feasibility and practicality should be primary factors" in determining reportable quantities pursuant to section 102." [2]

In this light, the Agency found it practical to adopt portions of the RQ adjustment methodology established under the CWA section 311 for adjusting RQs. This made sense since both Federal and State response agencies and the regulated community were familiar with the CWA section 311 reporting requirements. As a result, the five-level reporting categories were also adopted: 1-, 10-, 100-. 1000-, and 5000- pounds.

Unlike CWA section 311, which is solely concerned with the discharge of approximately 300 substances into navigable waters, CERCLA is a multi-media statute. Under CERCLA, a comprehensive notification system has been developed for releases of almost 700 hazardous substances into all environmental media--land, air, and water. In order for the Agency to develop a simple, understandable, and implementable notification system for releases of so many hazardous substances into all environmental media, one RQ was assigned to each individual hazardous substance listed under section 101(14) of the Act. To have assigned different RQs for different media would have been unworkable due to the complexity of such a system, as well as the fact that most releases occur into more than one medium and releasers would not always know exactly which media will be affected.

Generally speaking, the regulated community seems to have accepted the single RQ approach. Only a few chemicals have been brought to the Agency's attention by industry as a candidate for obtaining a dual RQ. Such a substance is PCBs, which has a proposed RQ of one-pound based on aquatic toxicity. Many utility companies feel that such a low RQ will result in over-reporting to the NRC, due to the large percentage of failures of small capacitors and transformers. This apparent burdensome reporting requirement coupled with the contention that most PCB releases are to land and not to water, lead these utility companies to request that the Agency consider a different RQ for PCBs for land releases. If the Agency were to adopt such an approach of setting RQs on the basis of the most prevalent release medium, releases to media posing greater hazards to public health, welfare or the environment may result for which the government does not receive the necessary notification to respond. The Agency is currently examining comments on this and other issues.

RQ Adjustments Methodologies Examined, But Not Used

Before arriving at the RQ Adjustment Methodology as proposed in the May 25, 1983, Federal Register Notice, the Agency examined a number of other strategies for adjusting RQs, such as Hazard Indices, Fate and Effects, and Worst Case Scenarios. All of these alternative approaches had disadvantages outweighing the benefits of adopting any of the particular strategies.

After extensive internal and external review, the Agency finally adopted an RQ Adjustment Methodology known as Selective Criteria Processing (SCP). Unlike the CWA section 311 RQs which were assigned on the sole basis of aquatic toxicity data, the SCP strategy looked at several other criteria, in addition to aquatic toxicity. The six primary criteria utilized in the SCP RQ Adjustment Methodology are: aquatic toxicity, acute mammalian toxicity (oral, dermal, and inhalation), ignitability, reactivity, chronic toxicity and carcinogenicity. These criteria were chosen in order to be responsive to CERCLA's mandate to protect human health (acute mammalian toxicity, chronic toxicity, and carcinogenicity), welfare (ignitability and reactivity), and the environment (aquatic toxicity).

Six separate scales were developed for the six primary criteria in order to assess the relative "hazardousness" of the particular hazardous substance.

Aquatic Toxicity

The five-level RQ scale developed for the CWA section 311 were retained for the CERCLA RQ adjustments. (See Table 1)

Acute Mammalian Toxicity

Three types of acute mammalian toxicity were evaluated: oral, dermal, and inhalation toxicities. A five-level scale was developed for each toxicity by determining an upper bound toxicity limit for the 5000 pound category and then using the same direct proportionality used in the CWA section 311 aquatic toxicity scales to arrive at the LC(50) and LD(50) values for each of the subsequent lower RQ levels. (See Table 2)

Oral Mammalian Toxicity

To arrive at the upper bound toxicity level for acute oral mammalian toxicity, the assumption was made that a small child is exposed to a toxic material under circumstances which allow him to take one swallow of the material. Experimental study shows that a child's swallow size amounts to 4.0 to 4.5 cubic centimeters. For a child weighing 15 kg, the appropriate calculation results in the oral toxicity of 300 mg/kg of body weight, assuming the ingested substance has a density of one. Next, a safety factor was added in order to allow for lower body weights and/or higher density substances. The resulting upper bound oral toxicity level was an LD(50) of 500 mg/kg of body weight.

It is interesting to note that applying the same set of factors to standard man(70 kg body weight, swallow volume of 21 cubic centimeters) also yields a value of 500 mg/kg of body weight.

A number of Agency toxicologists, as well as experts in the field of toxicity poisonings have reviewed and concurred with this basis for arriving at an upper bound oral toxicity level for the 5000 pound RQ level.

Dermal and Inhalation Toxicity

The upper bound toxicity limits of 200 mg/kg for dermal toxicity and 2000 ppm for inhalation toxicity were taken from the National Academy of Sciences (NAS) System for Evaluation of Hazards of Bulk Water Transportation of Industrial Chemicals.[3]

Ignitability and Reactivity

The scales for ignitability and reactivity (self reaction and reaction with water) were based on scales developed by NAS. (See Tables 3 and 4) Because small amounts (one pound) of ignitable and reactive substances rarely require federal response, the one pound RQ levels on each of the scales is left unused. Responses to such small releases are generally handled at the state or local levels.

Chronic Toxicity

The five-level chronic toxicity RQ scale and the hazardous substance assessments for chronic toxicity were performed by the Agency's Environmental Criteria and Assessment Office (ECAO) located in Cincinnati, Ohio. The chronic toxicity criterion was used because releases can have chronic effects over time. These evaluations use data on the minimum effective dose (MED) for repeated or continuous exposure and the severity of the effects of such exposure. (See Figure 1 and Tables 5 and 6)

Carcinogenicity

Carcinogenicity was used as a SCP primary criterion in adjusting RQs because of the danger of carcinogens to human health and the potential need for response to releases of carcinogenic material. The Agency's Carcinogen Assessment Group (CAG) performed the RQ assessments for known human and potential human carcinogens which were listed under section 101(14) of CERCLA. This assessment is a relative hazard ranking scheme based on a substance's carcinogenic potency and the strength of evidence of the substance's carcinogenicity using the International Agency on the Research of Cancer's (IARC) "strength of evidence" classification scheme. This criterion is undergoing internal Agency review and will be the subject of an upcoming rulemaking.

Secondary Criteria

In addition to the six primary criteria, a set of secondary criteria were developed which reflect possible mitigating environmental effects on a substance after its release. These secondary cirteria are three natural dissipation processes: biodegradability, hydrolysis, and photolysis. These secondary criteria are only applied after a substance has received a tentative RQ based upon the six primary criteria. See Table 8 for a list of the CERCLA hazardous substances whose RQ was adjusted on the basis of one of the secondary criteria.

RQ Assignments

Each hazardous substance is analyzed on the basis of the six primary criteria. If a hazardous substance poses a potential hazard based on more than one of these criteria, the "primary criteria" RQ selected is the lowest RQ value identified. This procedure will ensure that the federal government will be notified of the most serious potential hazard to the public health, welfare, and the environment; and is consistent with the fundamental philosophy that the RQs should serve as a trigger for notification and timely Federal response, if warranted.

After the "primary criteria" RQ has been determined, if the hazardous substance exhibits any of the three secondary criteria, the RQ is raised one level (e.g. 100 pounds to 1000 pounds). Figure 2 is a diagrammatic flow chart detailing this RQ assignment process.

Special Substances

As in all rulemakings, there are several anomalies which do not lend themselves to be easily incorporated into the existing system which generally applies to all other situations. Several CERCLA hazarous substances fall into this category, and therefore, must be treated differently from the other CERCLA hazardous substances listed under section 101(14). The three substances which will be discussed here are: (1) unlisted RCRA Wastes (Ignitable, Corrosive, Reactive, and Extraction Procedure Toxicity (ICRE) Wastes); (2) Radionuclides; and (3) Metals.

ICRE Wastes

RCRA hazardous wastes which are not listed as specific hazardous wastes, but which exhibit the characteristics of ignitability, reactivity, corrosivity, and extraction procedure toxicity, are CERCLA hazardous substances. These hazardous wastes were all given a statutory RQ of one pound under CERCLA.

Because the constituents and corresponding concentrations of ICR wastes are generally unknown, the application of the SCP process was impossible. As a result, an RQ of 100 pounds was proposed in the May 25, 1983, Federal Register Notice for those unlisted hazardous wastes exhibiting the characteristics of ignitability, reactivity, and corrosivity. The 100 pound RQ was selected by assuming that the ICR wastes, on the average, will fall in the middle range of the five RQ levels, i.e., 100 pounds.

The EP toxic wastes, on the other hand, have already undergone chemical analysis to determine the presence of 14 different contaminants and their corresponding concentrations. As a result, the SCP RQ adjustment process can be applied to such hazardous wastes to arrive at the appropriate RQ.

Radionuclides

Radionuclides are a CERCLA hazardous substances because they are designated as a hazardous air pollutant under the Clean Air Act section 112. Because radionuclides pose a different hazard from the other CERCLA hazardous substances, they must be treated separately. The RQ assignment for radionuclides requires a different RQ adjustment approach. Pounds is an inappropriate measure for radionuclide releases.

The Agency did not propose an RQ for radionuclides in the May 25, 1983, Federal Register Notice. Rather, comments were solicited on the following issues before a final RQ adjustment process could be solidified:

- Should radionuclides be designated generically, or should separate radionuclides be listed as CERCLA hazardous substances?
- Should the RQ for radionuclides be set on the basis of dose-equivalents for the generic designation, or should RQs be in activity levels for specific radionuclides?

Once the Agency has been able to thoroughly examine these options, a position on radionuclides will be taken and put forth in an NPRM for comment by the interested community.

Metals

A number of metals have been statutorily designated as CERCLA hazardous substances. Releases of massive forms of these metals, such as lead bars or ingots, however, generally do not pose the significant hazard to public health, welfare, or the environment, as does the release of finely divided lead particulates. Small metal particles can easily enter the food chain through many routes and, therefore, be ingested easily. Furthermore, small metal particles can also be inhaled without much difficulty. Larger forms of metal, however, rarely constitute such a serious health hazard.

With this in mind, the Agency decided not to require the notification of releases of massive forms of metals in which the metal particulates have a diameter greater than 100 micrometers (.004 inches). It is believed that particles of this size are not large enough to be respirable or react rapidly with air or water.

RQ Adjustment Results

As was mentioned earlier, approximately 60 percent of the CERCLA section 101(14) hazardous substances have adjusted RQs proposed in the May 25, 1983, Federal Register Notice. The remaining 40 percent of the section 101(14) hazardous substances (309 substances) are currently being assessed for carcinogenicity and chronic toxicity. These RQ adjustments will be the subject of a separate rulemaking scheduled for next summer.

The application of the SCP RQ Adjustment Methodology to the 387 hazardous substances whose RQs were proposed in the May 25, 1983, Federal Register Notice is as follows:

-- 177 substances received higher RQs;
— 28 substances [4] received lower RQs; and
-- 182 substances retained existing RQs.

It should be noted, however, that all RQs retain their statutory levels until new RQs are set at the time of final promulgation of the regulation.

Economic Impact

Since the May 25, 1983, NPRM raised the RQs for many of the CERCLA hazardous substances, the number of notifications currently required by one pound statutory RQs should be reduced. The likely cost savings for this reduction in notifications is expected to be about $2.7 million/year for the regulated community and about $16.5 million/year for the government. In addition, the notification burden is expected to be reduced by 57,000 hours based on the time estimated for gathering information on releases, reporting, and recordkeeping activities.

Conclusion

In summary, it should be noted that the May 25, 1983, Federal Register Notice: developed a sound, supportable, scientific basis for RQ adjustments; established a simple triggering mechanism for responses to emergency field situations; is deregulatory in nature, relieving the regulated community and the government of unnecessary reporting burdens of the one-pound statutory RQ's; and is the product of an "open rulemaking", resulting from extensive coordination with many parties both inside and outside the Agency (e.g. other Federal agencies, industry, and environmental groups).

FOOTNOTES

[1] Section 103(c) of CERCLA relates to notification of the existence of certain facilities that are or have been used for storage, treatment, or disposal of hazardous waste sites.

[2] Sen Rep. 96-848, 96th Cong., 2nd Sess. 29 (1980).

[3] " A Summary of Hazardous Substance Classification Systems" EPA/530/SW-177.

[4] The hazardous substances are all CWA section 311 hazardous substances. Only a CWA substance could receive a lower RQ since all other CERCLA section 101(14) hazardous substances had a statutory one pound RQ assigned by Congress.

TABLE 1

CATEGORIES FOR REPORTABLE QUANTITY ASSIGNMENTS PURSUANT TO CWA SECTION 311

RQ Pounds	Aquatic Toxicity	Category
1	LC_{50}[a] $<$ 0.1 mg/liter	X
10	0.1 mg/liter $\leq LC_{50} <$ 1 mg/liter	A
100	1 mg/liter $\leq LC_{50} <$ 10 mg/liter	B
1000	10 mg/liter $\leq LC_{50} <$ 100 mg/liter	C
5000	100 mg/liter $\leq LC_{50} <$ 500 mg/liter	D

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[a] "LC_{50}" refers to that concentration of material which is lethal to one-half of the test population of aquatic animals upon continuous exposure for 96 hours. [See 40 CFR Section 116.14]

Source: 43 FR 10492 (March 13, 1978).

TABLE 2

CATEGORIES FOR REPORTABLE QUANTITY ADJUSTMENTS BASED ON MAMMALIAN TOXICITY a/

RQ (Pounds)	Mammalian Toxicity (Oral)	Mammalian Toxicity (Dermal)	Mammalian Toxicity (Inhalation)
1	LD50[b] < 0.1 mg/kg	LD50 < 0.04 mg/kg	LC50[c] < 0.4 ppm
10	0.1 mg/kg ≤ LD50 < 1 mg/kg	0.04 mg/kg ≤ LD50 < 0.4 mg/kg	0.4 ppm ≤ LC50 < 4 ppm
100	1 mg/kg ≤ LD50 < 10 mg/kg	0.4 mg/kg ≤ LD50 < 4 mg/kg	4 ppm ≤ LC50 < 40 ppm
1000	10 mg/kg ≤ LD50 < 100 mg/kg	4 mg/kg ≤ LD50 < 40 mg/kg	40 ppm ≤ LC50 < 400 ppm
5000	100 mg/kg ≤ LD50 < 500 mg/kg	40 mg/kg ≤ LD50 < 200 mg/kg	400 ppm ≤ LC50 < 2000 ppm

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a/ For a detailed explanation of the derivation of these categories, see Background Document to Support the Notice of Proposed Rulemaking Pursuant to CERCLA Section 102(b).

b/ "LD 50" refers to that dose of a substance expected to cause the death of 50 percent of a defined experimental mammal population.

c/ "LC 50" refers to that concentration of a substance in the air that is expected to cause the death of 50 percent of a defined experimental mammal population.

TABLE 3

CATEGORIES FOR REPORTABLE QUANTITY ADJUSTMENTS BASED ON IGNITABILITY [a]

RQ (Pounds)	Ignitability (Fire)
1	No 1-pound RQs on the basis of ignitability
10	Pyrophoric or self-ignitable
100	FP_{cc}[b] < 100°F, BP[c] < 100°F
1000	FP_{cc} < 100°F, BP > 100°F
5000	100°F $\leq FP_{cc} \leq$ 140°F

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[a] For a detailed explanation of the derivation of these categories, see Background Document to Support the Notice of Proposed Rulemaking Pursuant to CERCLA Section 102(b).

[b] "FP_{cc}" refers to the flash point, the temperature at which a substance forms an ignitable mixture with the air at the surface of the substance, measured using the closed cup test.

[c] "BP" refers to the boiling point, the temperature at which a liquid boils.

TABLE 4

CATEGORIES FOR REPORTABLE QUANTITY ADJUSTMENTS BASED ON REACTIVITY a/

RQ (Pounds)	Reactivity b/	
	With Water	Self-Reaction
1	No 1 pound RQs on the basis of reactivity.	
10	Inflames e.g., Na, CaC_2	Extreme self-reaction; may cause explosion or detonation
100	Extreme reaction e.g., SO_3	High; may polymerize; requires stabilizer
1000	High reaction e.g., oleum	Moderate; contamination may cause polymerization; no inhibitor required
5000	Moderate reaction e.g., NH_3	Slight; may polymerize with low heat release

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a/ For a detailed explanation of the derivation of these categories, see Background Document to Support the Notice of Proposed Rulemaking Pursuant to CERCLA Section 102(b).

b/ Based on heat release.

TABLE 5

RATING VALUES FOR TOXIC EFFECTS

Rating	Effect
1	Enzyme induction or other biochemical change with no pathologic changes and no change in organ weights.
2	Enzyme induction and subcellular proliferation or other changes in organelles but no other apparent effects.
3	Hyperplasia, hypertrophy or atrophy, but no change in organ weights.
4	Hyperplasia, hypertrophy or atrophy with changes in organ weights.
5	Reversible cellular changes: cloudy swelling, hydopic change, or fatty changes.
6	Necrosis, or metaplasia with no apparent decrement of organ function. Any neuropathy without apparent behavioral, sensory, or physiologic changes.
7	Necrosis, atrophy, hypertrophy, or metaplasia with a detectable decrement of organ functions. Any neuropathy with a measurable change in behavioral, sensory, or physiologic activity.
8	Necrosis, atrophy, hypertrophy, or metaplasia with definitive organ dysfunction. Any neuropathy with gross changes in behavior, sensory, or motor performance. Any decrease in reproductive capacity, any evidence of fetotoxicity.
9	Pronounced pathologic changes with severe organ dysfunction. Any neuropathy with loss of behavioral or motor control or loss of sensory ability. Reproductive dysfunction. Any teratogenic effect with maternal toxicity.
10	Death or pronounced life-shortening. Any teratogenic effect without signs of maternal toxicity.

TABLE 6

CATEGORIES FOR REPORTABLE QUANTITY ADJUSTMENTS BASED ON OTHER TOXIC EFFECTS [a]

RQ (Pounds)	Composite Score
1	81-100
10	41-80
100	21-40
1000	6-20
5000	1-5

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[a] For a detailed explanation of the derivation of these categories, see Background Document to Support the Notice of Proposed Rulemaking Pursuant to CERCLA Section 102(b).

TABLE 7

Hazard	Carcinogenicity Classification		Potency Factor Group
High*	Sufficient**	and	1
Medium	Sufficient	and	2,3
	Limited	and	1,2
Low	Sufficient	and	4
	Limited	and	3,4

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* In some cases we might judge that factors such as genotoxicity, environmental persistence, and structure activity may warrant a limited, potency 1 agent to be ranked as a high hazard.

** Sufficient here means sufficient evidence with respect to human data and/or animal data.

TABLE 8

FINAL CANDIDATE LIST FOR UPWARD RQ ADJUSTMENTS (BIODEGRADABILITY, HYDROLYSIS, PHOTOLYSIS)

Hazardous Substance	Basis for Adjustment			Current RQ	Basis	Projected RQ
	B*	H*	P*			
Acetaldehyde (75-07-0)	X			100	I,R	1000
Acetic acid (64-19-7)	X			1000	311	5000
Acetic anhydride (108-24-7)	X	X		1000	311	5000
Acetone (67-64-1)	X			1000	I	5000
Acetyl chloride (75-36-5)		X		1000	AQTX	5000
Allyl alcohol (107-18-6)	X			100	311	CHRON TBA
Allyl chloride (107-05-1)		X		1000	311, T(orl), I	5000
Amyl acetate (628-63-7)	X			1000	311, I	5000
Aniline (62-53-3)	X			1000	T(ihl), 311	5000
Benzonitrile (100-47-0)	X			1000	311	5000
1-Butanol (71-36-3)	X			1000	I	5000
Butyl acetate (123-86-4)	X			1000	AQTX, I	5000
Butylamine (109-73-9)	X			1000	311, I	5000
Captan (133-06-2)		X		10	311	CHRON TBA
Cresol (1319-77-3)	X			100	AQTX	CHRON TBA
Cumene (98-82-8)	X			1000	I	5000
Diazinon (333-41-5)		X		1	311	10
Dipropylamine (142-84-7)	X			1000	I	5000
Ethyl acetate (141-78-6)	X	X		1000	I	5000
Ethyl acrylate (140-88-5)	X	X		1000	I	5000
Ethylenediamine (107-15-3)	X			1000	I, 311	5000

(continued)

TABLE 8 (Continued)

Hazardous Substance	Basis for Adjustment			Current RQ	Basis	Projected RQ
	B*	H*	P*			
Formaldehyde (50-00-0)	X			100	I	CHRON TBA
Hexachlorocyclopentadiene (77-47-4)		X	X	1	311	CHRON*
Isobutyl alcohol (78-83-1)	X			1000	I	5000
Malathion (121-75-5)		X		10	311	100
Methanol (67-56-1)	X			1000	I	5000
Methyl ethyl ketone (78-93-3)	X			1000	I	CHRON TBA
Methyl isobutyl ketone (108-10-1)	X			1000	I	5000
Methylmethacrylate (80-62-6)	X			1000	I	CHRON TBA
Mevinphos (7786-34-7)		X		1	311	10
Phenol (108-95-2)	X			1000	311	CHRON TBA
n-Propylamine (107-10-8)	X			1000	I, AQTX	5000
Pyridine (110-86-1)	X			1000	I	CHRON TBA
Quinoline (91-22-5)	X			1000	311	5000
Resorcinol (108-46-3)	X			1000	311	5000
Triethylamine (121-44-8)	X			1000	I, AQTX	5000
Vinyl acetate (108-05-4)	X			1000	I, 311	5000

NOTES:

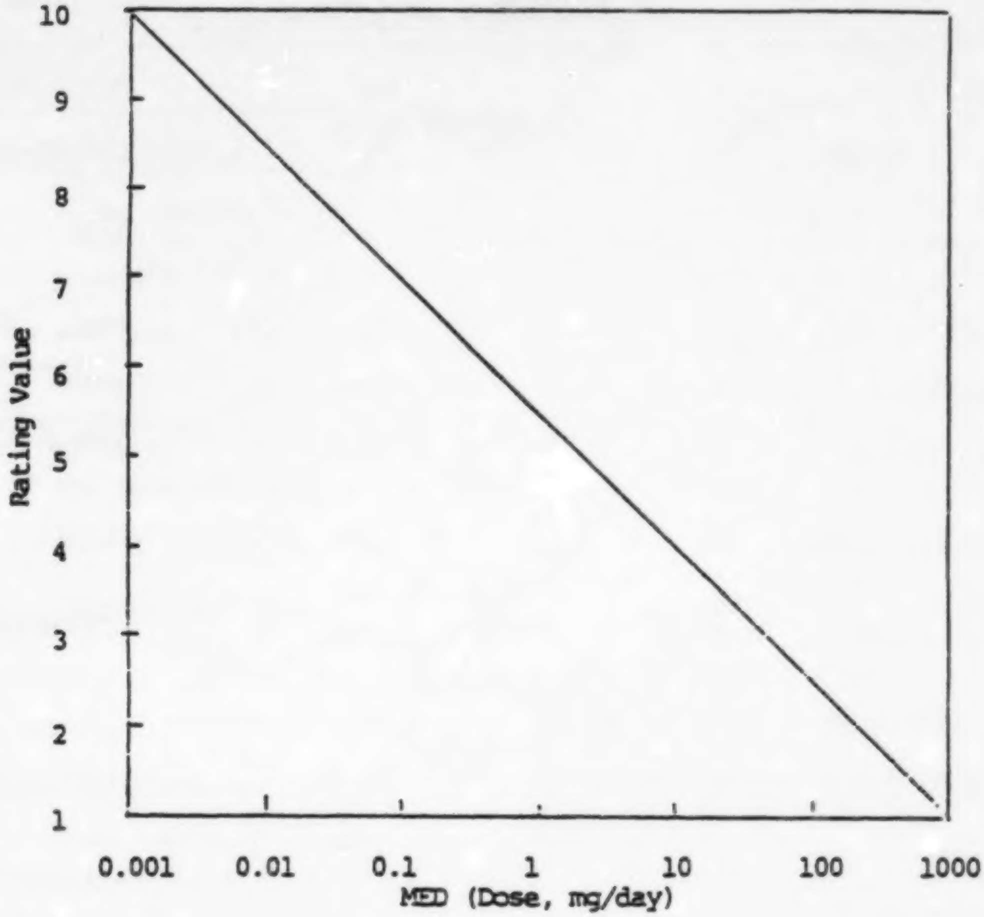
* B refers to biodegradability.

* H refers to hydrolysis.

* P refers to photolysis

(continued)

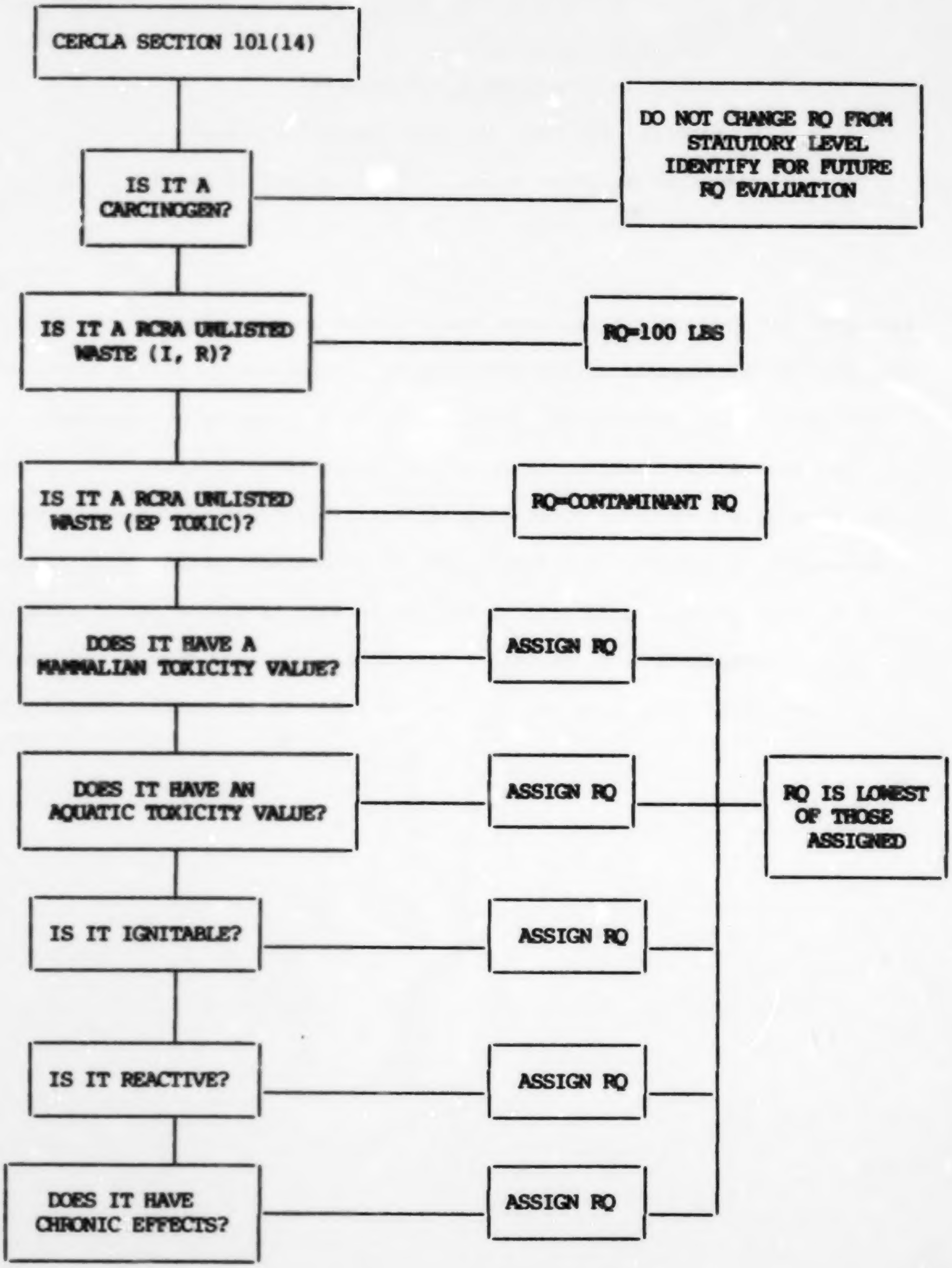
FIGURE 1



Note: All MED values of 1000 or greater are assigned a rating value of 1.

Dose Index/Rating Scheme

FIGURE 2


CERCLA SECTION 101(14)
IS IT A CARCINOGEN?
DO NOT CHANGE RQ FROM STATUTORY LEVEL IDENTIFY FOR FUTURE RQ EVALUATION
IS IT A RCRA UNLISTED WASTE (I, R)?
RQ=100 LBS
IS IT A RCRA UNLISTED WASTE (EP TOXIC)?
RQ=CONTAMINANT RQ
DOES IT HAVE A MAMMALIAN TOXICITY VALUE?
ASSIGN RQ
DOES IT HAVE AN AQUATIC TOXICITY VALUE?
ASSIGN RQ
RQ IS LOWEST OF THOSE ASSIGNED
IS IT IGNITABLE?
ASSIGN RQ
IS IT REACTIVE?
ASSIGN RQ
DOES IT HAVE CHRONIC EFFECTS?
ASSIGN RQ

RQ ADJUSTMENT STRATEGY

Chemical Spill Management:

Research Problems and Practical Applications

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Abstract

The bridge between pure research and practical application has long been the domain of the technologist. Often communication between the end user and the researcher is either poor or nonexistent. Many fields suffer from this problem, and chemical spill management is no exception. Seldom does the research chemist or biologist have the opportunity to observe a chemical spill incident first hand. The result is that a number of problems go unobserved and hence never become a topic of serious study. The following paper will attempt to address this problem through a discussion of practices, experiences, and perceived research needs in the spill management area.

Chemical Spill Management

Research Problems and Practical Applications

Over the past several years, industry and government have made significant and substantial investments in the area of hazardous chemical spills research. In general, the researcher, particularly at the university level, does not have the opportunity to observe the results of their efforts in the field. This is due to the random nature of the events and their locations. This handicap limits the creativity that could otherwise be applied to developing new approaches for mitigating the effects of spills. Thus, research activities are somewhat hampered.

Fundamental to generating research funding is the need to identify specific problems that must be solved. This need is highly dependent on the perception of the problems by the funding source. Government research goals and approaches are characteristically broader to scope than industry. As a result governments are often in the position of funding high risk work or work which may produce limited immediate practical results. Industry on the other hand is generally motivated to search for solutions to pressing problems. Hence, research investments are made based on the practical benefits of the results.

Aside from accident prevention, industries' principal concern in chemical spill research is to reduce the costs of a spill. Factors contributing to the total cost of an accident are variable and often difficult to isolate. The major factors are usually highly dependent on health effects and environmental damage.

Perhaps the greatest cost of an accident is created by third party civil suits. For example, litigation pending for one single rail accident has approached $1 billion. Settlements for exposure cases can approach $2 million even when exposures show no acute effects.

From an industry perspective, the most valuable research will produce results which will directly reduce the potential for this kind of liability. Obviously, accident prevention would represent the most effective solution to the spills problem. The multiplicity of factors relating to accident causes, however, limits the complete effectiveness of this approach.

Elimination of the chemical hazard is a viable option. This can be accomplished in three ways: 1) identify that the chemical does not represent a threat to public health, 2) insure that chemical spills do not occur around people, and 3) eliminate the chemicals' ability to do harm to the public.

Option 1 represents high risk research as previously defined. The state of the art in toxicological research is such that toxicity studies often create more questions than answers. Lack of agreement on the conduct and interpretation of animal studies strongly suggests a need for comprehensive basic research. Finally there is no guarantee that a substance will be found non-hazardous.

Moving hazardous material activity away from population centers, option 2, is attractive particularly when new facility construction is contemplated. Studies have been conducted concerning the feasibility of this option; however, history has demonstrated that when an industrial facility or transportation system is developed, people will settle around it. Hence the risk is not eliminated but deferred.

Eliminating the capacity to do harm appears to have the greatest potential for the immediate reduction of spill costs. This represents an area of great industry interest.

Events surrounding the response to a chemical can be broadly classified into three phases. The first involves initial response. During this phase, accident assessment, hazard identification and acute hazard mitigation are the principal activities. The second phase involves wreck clearing and gross cleanup operations. This generally involves debris removal and cleanup of large spills such as standing pools of chemical liquids. The last phase can be viewed as extended cleanup. During this period, hard to recover materials are removed. This includes contaminated soils, water and groundwater. Extended cleanup can take from months to years.

Research needs, as perceived by industry fall neatly into the three spill response phases. Under phase I, first response, the principal needs are in public and private response personnel training, protective equipment and spill damage assessment techniques.

Education of first response groups is of critical importance. The best information available is useless in the hands of an untrained responder.

Research and development in this area should include the potential for and development of computer simulations.

Spill assessment may take many forms. Remote sensing techniques need to be explored in greater detail. Predictive modeling of chemical behavior is currently in the infant stages; however, continued development of his tool will greatly increase the safety and efficiency of spill response.

Personal protective equipment is uncomfortable, bulky and often difficult to use. Research needs include extending the responders work time in a toxic atmosphere, mechanisms for eliminating heat exhaustion, as well as new designs for fully encapsulated suit to enhance vision and dexterity. The development of a single fabric effective against all substances would greatly reduce the potential for response related injuries.

Phase II needs include more effective methods for collecting and stabilizing a spilled substance. New techniques for plugging leaks are also needed. Often, accident mitigation is delayed for weeks because of fire and the threat of explosion prohibit activity on sight. Better and more effective firefighting tools are needed.

Within the last phase, extended cleanup, the most difficult problems are related to extraction of chemicals from soil, surface water and groundwater. A complete understanding of chemical behavior in each of these compartments is of major importance. Alternative methods to mechanical techniques are desperately needed. The cost of mechanical removal methods for chemicals in low concentrations is extremely high and their effectiveness low. Biological and chemical alternatives need greater attention.

The foregoing represent just a few of the areas in need of greater research attention. While the principal motivating factors for industry research are to reduce spill costs, these costs are directly related to health and environmental impacts. Research into reducing the cost of all phases of spill response will inherently reduce the health and environmental consequences of a hazardous material spill.

POOR

QUALITY

ORIGINAL